Text-Books of Physical Chemistry

EDITED BY

SIR WILLIAM RAMSAY K.C.B., F.R.S.

AND

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TEXTBOOKS OF PHYSICAL CHEMISTRY

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A SYSTEM OF PHYSICAL CHEMISTRY

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A SYSTEM OF PHYSICAL CHEMISTRY

BY

WILLIAM C. McC. LEWIS, M.A. (R.U.I.), D.Sc. (Liv.)

BRUNNER PROFESSOR OF PHYSICAL CHEMISTRY IN THE UNIVERSITY OF LIVERPOOL

IN THREE VOLUMES

VOLUME II

THERMODYNAMICS

THIRD EDITION

NEW IMPRESSION

WITH DIAGRAMS

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PREFACE TO THIRD EDITION OF VOLUME II

IN this edition the opportunity has been taken of making certain corrections which have been kindly brought to my notice by various correspondents. In addition a certain amount of new material has been incorporated so as to bring the book up to date as far as possible. The principal additions are: in Chapter VII, the e.m.f. method of determining the transport number of an ion as employed by MacInnes and Parker, an account of the investigation of Richards and Daniells on thallium amalgam cells, and Tolman's work on centrifugal cells; in Chapter VIII, an extended section dealing with ionic activity and ionisation, chiefly the work of the American School of Physical Chemistry. The problem of the activity of undissociated molecules is also considered. In Chapter XI, a résumé of the experimental evidence for Donnan's theory of membrane equilibria is given, and a fairly full account of the concept of the micelle in electrolytic colloids.

W. C. McC. LEWIS.

Muspratt Laboratory of Physical
and Electro-Chemistry,
University of Liverpool, *October*, 1920.

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A SYSTEM OF PHYSICAL CHEMISTRY

VOLUME II

CONSIDERATIONS BASED UPON THERMODYNAMICS

CHAPTER I.

Elementary Consideration of the Principles of Thermodynamics.

The science of thermodynamics deals with the laws and relationships which govern the quantitative transformations of *energy* of one sort into energy of some other sort during physical or chemical changes in a system. The name suggests the mutual relation of heat and motion, but the principles involved have a much larger scope, and may be applied under given conditions to all forms of energy. The characteristic feature of thermodynamics is that it permits us to deal with energy changes involved in a physical change of state, or in a chemical reaction without in any way requiring information regarding the *molecular mechanism* of the process under investigation. The conclusions which we shall arrive at on the basis of thermodynamics are thus independent of any molecular hypothesis we may have formed in respect of the process. This, it will be seen, is in many ways a very great advantage. It means that the conclusions of thermodynamics are quite general, and will remain true even if our views regarding the actual mechanism of the process considered from a molecular standpoint were to undergo radical change. Of course it will be seen as the converse of this that thermodynamical reasoning and conclusions, although true and general, do not tell us anything of the mechanism involved in a given process. This is naturally a considerable drawback, for advances in theoretical treatment seem to be most easily made along mechanical lines of thought, *i.e.* with the aid of molecular hypotheses. At the present time, therefore, the line of attack upon any problem which promises to be most successful is, in general, that in which we make simultaneous use of both generalised principles (thermodynamics) and the specialised principles (such as the Kinetic Theory). In Vol. I. the problems of

equilibrium in physical and chemical systems, and the behaviour of systems not in equilibrium, have been studied from a molecular standpoint. In the present volume we shall study the same problems from the standpoint of thermodynamics, bringing out as far as possible the general relation of thermodynamical conclusions to the conclusions drawn with the help of the Kinetic Theory. It is, of course, necessary first of all to obtain some information respecting the general ideas underlying the science of Energetics or Thermodynamics, and this matter forms the subject of the present chapter.

The classical theory of thermodynamics may be said to rest upon two main laws, or fundamental principles, known as the First and Second Laws respectively. Recently another principle has been brought forward by the noted German scientist, Professor Nernst, of Berlin, which seems likely to ultimately take its place as a third law. This principle and its applications are discussed at the conclusion of our study of affinity (Chap. XIII.). For the present we shall confine our attention to the First and Second Laws.

The First Law of Thermodynamics.

This law is simply a statement of the principle known as the Conservation of Energy, according to which energy can be changed from one form to another, but can never be destroyed. Before discussing this let us consider briefly what we mean by the term "energy".

When a body or system can do *work* against a force it is said to possess energy. How are we to obtain a *measure* of this energy? This is effected by regarding the decrease in energy as equal to the work done. When the energy arises from motion—say of the molecules of a system, or of the system as a whole in space—it is called Kinetic Energy. When it arises from the relative position of bodies it is called Potential Energy. From the standpoint of thermodynamics, however, we do not distinguish the *origin* of energy whether it be kinetic or potential (as this would really involve molecular hypotheses); instead, we deal simply with the energy possessed by a body, or more frequently with the energy gained or lost by a system when the system undergoes a given change, without specifying more closely whether the energy thus lost or gained is kinetic or potential in nature. It is important to notice that although we can mentally conceive of the idea of a given substance or system possessing energy, we are unable to give this a *numerical* value. What we can do, however, is to ascribe a numerical value to the *change* in energy involved in a given process; and it is with such *changes of energy, i.e.* either gain or loss of energy, that thermodynamics deals. A simple illustration of a mechanical nature will make the distinction clear. Suppose a body having the mass of 1 gram falls a distance of 1 meter towards the earth under the action of gravity. The *loss* of potential energy sustained by the body in thus altering its position is 1 gram-meter, this being the work done in the change considered. We do not know the absolute value of the poten-

tial energy of the body in its initial position, but we do know that in its final position it has lost an amount, 1 gram-meter. Now, the study of mechanics has made us familiar with the idea that the term "work," or "energy," is a composite one, being always expressible as the product of two terms, one term being known as the "intensity factor," the other as the "capacity factor". The simplest conception of work or energy is to regard it as the product of force into distance. The force is the "intensity factor," the distance the "capacity factor". A force has the dimensions[1] $\frac{ML}{T^2}$, and a distance the dimension L, so that energy or work must have the dimensions $\frac{ML^2}{T^2}$. Even when the actual energy is not simply force × distance it must still have the dimensions above ascribed to it. Thus let us consider another sort of simple process in which work is done and the equivalent energy expended, namely, the isothermal expansion of a gas against the atmosphere or other pressure. Suppose the initial volume of the gas was v c.c., and the increase in volume is a very small one dv. Suppose p is the atmospheric pressure (in dynes per square centimeter). Let us suppose the gas is in a cylinder fitted with a weightless, frictionless, movable piston as in Fig. 1. The surface area of the piston may be A cm.^{2}. In the equilibrium state the pressure above and below the piston must be identical $\left(i.e.\ p\frac{\text{dynes}}{\text{cm.}^2}\right)$. Under these conditions the piston would remain motionless for an infinite time. Suppose, however, that the gas pressure, *i.e.* the pressure exerted upon the lower side of the piston, is something greater than p. The gas will tend to push the piston outwards. Suppose it does so through an infinitely small distance dx. The work done = force × distance = $(p \times A) \times dx$, but $Adx = dv$; $\therefore$ work = pdv. Now, in performing this expansion against the external pressure p, the gas has done work upon the surrounding atmosphere, or, in other words, it has caused energy to be expended. We shall speak of the source of this energy in a moment. The expression for the work done is simply the pressure into the increase in volume, namely, pdv. We see that this term actually represents work, for it has the correct dimensions, namely, $\frac{ML^2}{T^2}$, and may be ultimately expressed as force × distance. The source of the energy which has been used in the work of expansion if the temperature has been maintained constant, is the heat which has

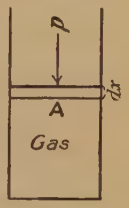


Fig. 1.

[1] Force is mass × acceleration = $\frac{\text{mass} \times \text{velocity}}{\text{time}}$ and velocity = $\frac{\text{length}}{\text{time}}$. Denoting the dimensions of mass by M, length by L, and time by T, we can write the dimensions of force as being $\frac{M \times L}{T^2}$.

been drawn from the surroundings. This is an "isothermal expansion". If we had enclosed the gas in a "heat tight" case and allowed it to do work we would have found that its temperature would have fallen (though only to an infinitely small extent, if the expansion was infinitely small). In the latter case the work is done at the expense of the heat energy of the gas itself. By this heat energy we mean the kinetic energy of the molecules, for heat, properly speaking, does not reside *in* a system, being transferable from one system to another, but always undergoing transformation into something else (*i.e.* say, into kinetic energy of the molecules) after its addition to a system. It will be observed that in order to keep the temperature of the gas constant whilst expansion proceeds we have assumed that heat is given to the gas from its surroundings in order to compensate for the cooling effect of the expansion itself. This really involves the principle of the First Law, for what we have actually done is to transform heat energy into mechanical energy, the gas simply acting as the medium.

Besides heat and mechanical energy we are acquainted with many other forms of energy, *i.e.* electrical energy, magnetic energy, radiant energy, surface energy (*i.e.* the product of surface tension of a liquid into the area of the surface), and chemical energy. All these must ultimately be expressible by the expression $\frac{ML^2}{T^2}$. Now, the First Law deals with the transformation of any kind of energy into any other kind, and according to the law, when a certain amount of one kind disappears an exactly equivalent quantity of some other kind must appear. When a bullet strikes a target there is heat produced, the amount of heat being equivalent to the kinetic energy which the bullet possessed just before striking. If we lose 100 ergs of mechanical energy in some process we must gain 100 ergs in some other form—heat, for example; for energy can neither be created nor destroyed as a whole. This is why perpetual motion is impossible; it is more accurate to say that in the experience of mankind, no instance of perpetual motion has been recorded, and we have therefore concluded that such is impossible. This is stated by the First Law. The First Law is a law of experience, just as the Second Law is, as we shall see later. Assuming the validity of the First Law, we are led to make a determination of the so-called "mechanical equivalent of heat," an experiment carried out in the first instance by Joule, and later by Rowlands and others. Joule's determination of the equivalent consisted in placing some water in an isolated vessel and then rapidly rotating a paddle in the water. He observed that the temperature of the water rose—just as Rumford, many years previously, had observed that in the boring of a cannon the friction caused the metal to become extremely hot. With Joule's arrangement it was possible to obtain a quantitative connection between the mechanical work done in stirring, and the heat added to the water, as evidenced by the rise in temperature. The paddle was worked by means of a falling weight, the working agency being therefore gravitation. Frictional effects were reduced as far as possible. Knowing the weight of the

falling body, and the distance through which it fell, the amount of work done by gravitation can be directly obtained. If, now, the rise in temperature of the water is measured, the heat capacity of the water being known, the amount of heat in calories generated by the motion of the paddle is also obtained. If we neglect or allow for friction and other disturbing effects we can find how many mechanical work units, *i.e.* ergs, are equivalent to 1 heat unit, *i.e.* 1 calorie. Joule found that 1 calorie $= 4{\cdot}2 \times 10^7$ ergs (approx.). Rowlands's more accurate determinations agreed closely with Joule's value. In the cases where work is done by the expansion of a system (against pressure), we have assumed that the temperature *can* be kept constant by adding the requisite amount of heat which is transformed into mechanical work (pdv) via the system considered. That is to say, we assume the validity of the First Law regarding the mutual transformation of heat into mechanical energy, and *vice versâ*. To give precision to our statement of the First Law we want to be able to express it algebraically. For this purpose let us think of some system (solid, liquid, gaseous, homogeneous or heterogeneous) which undergoes some physical or chemical change. In general there will be associated with this *matter* change the following *energy* changes :—

(1) A certain amount of heat may be absorbed or evolved by the system.

(2) A certain amount of external work is either performed *by* the system or upon it (by the surroundings).

(3) The internal energy of the system may have increased or decreased. (This naturally possesses a complicated mechanism. Often it can be regarded as due to changes in the relative position, rate, and kind of motion of the molecules. We are, however, not concerned here with the mechanism of changes going on in the interior of a system. We simply consider the fact itself that the internal energy, or, as it is often called, the total energy, has altered in a given process.) No matter what the process itself may be, the First Law tells us that decrease in internal energy (supposing there to be a decrease, which *decrease* we denote by + U) must be equal to the external work done, namely, A (say due to an increase in volume against a pressure) plus the amount of heat evolved or lost (call the heat absorption + Q, then − Q represents the heat evolved). Algebraically this statement takes the form—

$$U = A + (-Q) \quad \text{or} \quad U = A - Q \quad . \quad . \quad . \quad (1)$$

Consider a system in which a chemical change occurs without alteration in volume, and without doing any form of external work. Suppose the internal energy decreases by the amount U. This energy leaves the system in the form of heat evolved, which is denoted by the term $-Q_v$, the suffix v indicating that the volume has been kept constant. Then

$$U = -Q_v.$$

Even when the reaction cannot be carried out without a change in volume (say an increase in volume) the heat equivalent of the work

done by the system in expanding, against the atmosphere, say, can be calculated, and this amount is added to the observed heat evolved to give the quantity $-Q_v$. The symbol Q_v must not be confused with Q. As a matter of fact, Q is in many cases (though not always) a much smaller quantity than Q_v. Q is often called a "latent heat". If a process occurs and does work A of any kind (not necessarily mechanical), and at the same time the internal energy of the system diminishes by the amount U, then the term Q simply stands for the *difference* of the two terms A and U. Q is not a measure of U at all. In some cases (A – U) may be almost zero, *i.e.* A and U may be nearly equal, and therefore Q may be nearly zero, and this may be so when both A and U (or $-Q_v$) possess large numerical values. In other cases, however, U (or $-Q_v$) may be very small, in which case the work done (A), which may be great, is at the expense of the heat taken in, *viz.* Q. This is very nearly realised in the work done by an expanding gas. Naturally these terms must be expressed in the same units, say calories. Note also that in the above nomenclature + U represents a *decrease* in the internal energy and – U therefore represents an *increase* in the internal energy of the system. (The sign here has significance with respect, not to the system itself, but to the surroundings. A gain in energy to the surroundings must mean loss in energy to the system.) The term + A represents external work done *by* the system on the surroundings, – A represents external work done *upon* the system by the surroundings.

+ Q represents heat added to or absorbed by the system.
– Q represents heat taken from or evolved by the system.

The Concept of *Maximum* Work.

In returning to the question of the work done in the expansion of a gas, it will be observed that we considered an increase in volume so small that the pressure of the gas had remained constant. Suppose now that we consider a finite change in volume from v_1 to v_2. Since the system is a gas we know that on increasing its volume its own pressure will decrease. The work which can be got out of the gas will depend upon the opposing pressure, and it is clear that it depends upon the magnitude of this opposing pressure whether the gas can expand up to v_2 or not. If the opposing pressure is always less than that possessed by the gas, even at the large volume v_2, the piston on being released will move rapidly from v_1 to v_2, the work done being $p(v_2 - v_1)$. But this work is not in any sense a definite amount characteristic of the pressure of the gas, for p is the external opposing pressure. It is evident that the work done by the gas can vary (*even when expanding between the same volume limits*), *depending on the values of the opposing pressures.* If the opposing pressure is zero the work will be zero. Is there an upper limit to this work term? To get at this we have to consider the work done from the standpoint of the pressure possessed by the gas itself. Let us first of all ask the question, What are the conditions under which a gas

must be placed in order that a very small expansion dv may be accompanied by a *maximum* output of work? *The necessary condition which must be fulfilled so that the gas can do a maximum amount of work in expanding by dv is that the external pressure should be less than the pressure (call this now p) possessed by the gas by an infinitely small amount dp.* If we imagine the outer pressure (that of the atmosphere) to be $(p - dp)$, then the pressure of the gas p will be *just* able to overcome this outer pressure. The work done is $(p - dp)\ dv$, or, what is the same thing, pdv, for the product $dp \,.\, dv$ is only of the second order of magnitude, being the product of two infinitely small quantities. If the external pressure had been exactly equivalent to p the piston would have remained motionless. If the external pressure had been $p + dp$ the piston would have moved inwards infinitely slowly, the work done *upon* the gas being $-(p + dp)dv$ or $-pdv$, the negative sign denoting a decrease in the volume of the gas. It will be seen that under the above pressure conditions the process is a *reversible* one in the sense that for the same volume change (in one case an increase, in the other a decrease) the work done is represented by the same *numerical* magnitude $\pm pdv$. When the expansion takes place in this way it is accompanied by maximum work, so that the production of maximum work is the characteristic of a process which is being carried out in a *reversible* manner. We shall speak at greater length of reversible processes later on. It may here be noted that since the external pressure is so arranged that the pressure possessed by the gas is just able to overcome it, the expansion through dv must take place infinitely slowly. Hence the gas does not get up momentum which on stopping would be transformed into heat of indeterminate amount. No friction effects take place either on the outgoing or return journey. The process can, therefore, be repeated an infinite number of times without any *permanent* drain on the energy resources of the system and surroundings. As already mentioned the source of the energy which enables the gas to expand and do work and yet keep the temperature constant is then the "heat content" of the surroundings. In a reversible process the heat taken in from the surroundings during the volume expansion is *exactly* the same in amount as the heat given back to the surroundings when the gas contracts isothermally and infinitely slowly to its original position. If there had been a net loss or gain of heat, say, as a result of the total operation, the process is called an irreversible one, for on completing the process isothermally there would be a permanent change in the "heat content" of the system and surroundings. A reversible process is essentially one in which the change takes place in a known and definite manner, there being no "accidental" energy transformations taking place, dependent on the *path* followed, *i.e.* dependent on the physical structure, shape, or properties of the system. Of course a reversible process is only a limiting case. It cannot be realised in practice since a "frictionless piston," an "infinitely slow process" with a "pressure difference infinitely small" on the sides of the piston, is only *mentally* realisable. The significance of reversible processes and maximum work

production will be clear when we come later to study the Second Law of Thermodynamics.

We have been considering how the maximum work can be done by a gas expanding through an infinitely small volume dv. We have now to consider the maximum work produced when a gas undergoes a measurable volume increase from v_1 to v_2. We know that the pressure of a gas falls as the volume increases. We cannot, therefore, use the expression $p(v_2 - v_1)$ as the expression for the maximum work. In fact, we cannot think of the external pressure on the piston remaining constant. It must also continuously decrease in the same proportion as that of the gas pressure itself, being at any stage only less than that of the gas itself by the infinitely small amount dp. To find out what the maximum work is we have to suppose the total expansion carried out in a series of infinitely small steps, each being represented by the product of the existing pressure into a small volume increase dv and then add them all together. Analytically we can express it thus—

Total maximum work done in expansion from v_1 to v_2

$$= \int_{v_1}^{v_2} p\,dv.$$

In order to carry out this integration we must know p in terms of v. If the system is gaseous we can make use of the gas law, *viz.*—

$$pv = n\mathrm{RT}$$

where n is the number of gram-molecules of gas in volume v, and R is the gas constant. Substituting this value of p in the integral we obtain—

$$\text{Work done} = \int_{v_1}^{v_2} p\,dv = \int_{v_1}^{v_2} n\mathrm{RT}\frac{dv}{v} = n\mathrm{RT}\int_{v_1}^{v_2}\frac{dv}{v}$$

$$= n\mathrm{RT}\log\frac{v_2}{v_1}, \text{ (where log} = \log_e\text{)}.$$

The maximum work done when *one* gram-mole of gas expands isothermally and reversibly from v_1 to v_2 is therefore—

$$\mathrm{RT}\log\frac{v_2}{v_1}.$$

Since we have already assumed the gas laws for the system considered we can evidently write this expression in an alternative form, *viz.*—

$$\text{Maximum work per gram-mole} = \mathrm{RT}\log\frac{p_1}{p_2}.$$

It may be pointed out, parenthetically, that in the isothermal evaporation of a liquid we have a case in which there may be a large volume change, the pressure remaining constant, namely, the pressure of the saturated vapour. Suppose a cylinder fitted with a piston contains some liquid and saturated vapour. Let us consider what is the value of the maximum work which will be done when one gram-mole of the liquid is vaporised. We suppose that there is more than one gram-mole

of liquid present to start with, so that throughout the whole operation the vapour is saturated. Suppose the piston (Fig. 2) is raised in a reversible manner, *i.e.* infinitely slowly, the pressure outside being very nearly the value of p, the pressure of the saturated vapour (*i.e.* the pressure outside the piston) is $p - dp$. The process is assumed to take place isothermally, and hence heat must be continuously supplied from the outside to supply that which has become latent in the process of vaporisation. If the increase in volume of the vapour corresponding to the production of one gram-mole of vapour is V, and the decrease in the volume of liquid at the same time is v, the maximum external work done by the system as a whole is $p(V - v)$. In general we can neglect v compared to V. The work is then pV. Further, if we assume that the vapour obeys the gas laws, we can write maximum external work done in vaporising one gram-mole of gas $= pV = RT$ where R is 1·985 calories and T the absolute temperature. It may be noted that the piston may start from any level, *i.e.* from the surface of the liquid itself or from any position above, for we only deal with *change* in V, not with the initial volume actually possessed by the system. The student will note that it has not been necessary to take into consideration the actual value of the heat quantity added. One must be careful, however, not to imagine that the heat added and the external work done are identical in this case. In fact, the heat added is very much greater than the heat equivalent of the external work done.[1] There has been a considerable change in the internal energy of the gram-mole of liquid due to its vaporisation. In the case of water, for example, the heat required to vaporise one gram at 100° C. is about 540 calories. The external work done (A) against the atmosphere is about 40 calories, the so-called "external latent heat," leaving 500 calories as the "internal latent heat". This term represents the change in U which has taken place in the transforming of one gram of liquid water into water vapour. For the whole process—

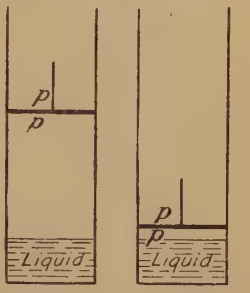


FIG. 2.

$$U = A - Q \quad \text{or} \quad Q = A - U.$$

In the above we have, however, only been dealing with the magnitude of the single term A.

[1] This case should be contrasted with the previous one, namely, the production of maximum work by the expansion of a perfect gas. In the case of the gas, the heat which had to be added in order to keep the temperature of the gas constant during the expansion was quantitatively converted into the work done. In the case of a perfect gas, as we shall see later, there is no change in the *internal* energy when expansion takes place. That is, $U = 0$ and therefore $A = Q$, *i.e.* the heat added from the surroundings is exactly equivalent to the work performed by the gas. In short, the gas acts as a transformer of heat into work.

Maximum Osmotic Work in Solutions.

We are already acquainted with the fact that a solution, such as a dilute sugar solution, obeys the gas laws. Let us regard this as an experimental fact—as it has indeed been shown to be. Now, the process of *diluting a solution* is a familiar one, and we can see that, under certain conditions, this is analogous to diluting a gas, *i.e.* increasing the volume of the gas. It seems justifiable, therefore, to conceive of work being done by the solution, or rather by the solute in the solution during dilution, for we have here the two necessary factors, pressure (*i.e.* osmotic pressure) and volume change. In order to make the dilution process as mechanical as possible, and thereby bring out the close analogy to the expansion of a gas, we have recourse to a device called the semi-permeable membrane, with which we are already familiar in our previous discussion of solutions. The semi-permeable membrane allows solvent to pass freely through it, but not the solute, *i.e.* the solute can exert its osmotic pressure *against* the semi-permeable membrane. For our present purpose of calculating *maximum* work it does not matter in the least whether we can realise in practice such a membrane or not, for we are considering a limiting case in either event. As a matter of fact, however, several semi-permeable membranes (or practically semi-permeable membranes) have been used in practice, notably that consisting of copper ferrocyanide, deposited in the walls of a porous pot which, while it allows water to pass freely through it, altogether prevents the passage of sugar dissolved in the water.

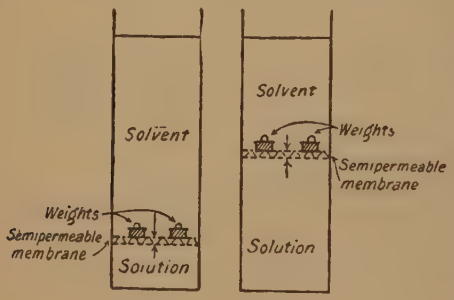


Fig. 3.

Suppose, now, we had a quantity of solution in a cylinder, and above the solution a layer of pure solvent, a semi-permeable membrane being placed between the two layers just where the solution meets the solvent (see Fig. 3). To keep the semi-permeable membrane motionless, we must imagine weights placed upon it so as to just balance the osmotic pressure of the solute in the solution which is tending to press the membrane out in exactly the same manner as a gas tends to push an *im*permeable piston out. To obtain the maximum work which could be done by diluting the system from volume V_1 to volume V_2, that is, in ordinary chemical nomenclature from "dilution" V_1 to "dilution" V_2, we suppose the semi-permeable membrane or piston to rise infinitely slowly, the pressure due to the weights being adjusted so as to be less than the osmotic pressure by the infinitely small quantity dP. We must imagine the weights continually to decrease in number so as to

keep pace with the continuously decreasing osmotic pressure of the solution, for of course the osmotic pressure of the solution decreases as the dilution increases.

As the membrane moves up, solvent passes through it, *no* pressure difference being set up on the two sides of the membrane, so far as the solvent is concerned, for the membrane is perfectly permeable to the solvent although impermeable to the solute. It may be pointed out that if no weights, *i.e.* no opposing pressure, had been placed upon the membrane, the latter would move instantaneously up through the solvent, *no work* being done thereby ; just as we saw no work was done when a gas expanded into a vacuum. We are at present dealing, however, with the exactly opposite limit, namely, the production of maximum work. As in the case of the gas, the maximum work for the whole volume or dilution increase is given by the expression—

$$\int_{V_1}^{V_2} P dV$$

where P denotes the osmotic pressure of the solution. To evaluate this integral we must know P in terms of the dilution. This is given by the experimental fact that osmotic pressure follows the gas laws, *viz.*—

$$PV = RT \quad \text{or} \quad P = \frac{RT}{V} = RTC$$

when C is the reciprocal of dilution and represents the concentration of the solute in the solution, $C = \frac{1}{V}$. To be able to give a definite numerical value to R we must deal with a certain mass of solute, say 1 gram-mole, in which case R = 1·985 calories. The *maximum osmotic work* done by the system in diluting 1 gram-mole of solute from a dilution V_1 to a dilution V_2 is given by the expression—

$$RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \log \frac{V_2}{V_1}.$$

If we dealt with *n* gram-moles of solute the maximum osmotic work would be *n* times as great, *viz.*—

$$nRT \log \frac{V_2}{V_1}.$$

Using osmotic pressure terms instead of volume terms, since we know the relation between them, namely, $P = \frac{RT}{V}$, the above expression can be written for the case of one gram-mole as—

$$\text{Maximum osmotic work} = RT \log \frac{P_1}{P_2}$$

or since $V = \frac{1}{C}$,

$$\text{Maximum osmotic work} = RT \log \frac{C_1}{C_2},$$

where C_1 is the initial concentration of the solution and C_2 its final concentration. It is well to notice, however, that we have employed the gas law expression in dealing with these solutions. The accuracy of the expression is, therefore, limited by the range of applicability of the gas laws to the solutions. That is, the above expression gives the maximum osmotic work for dilute solutions only.

External Work Defined as a Change in Free Energy of the System and Surroundings.

When a body does work at constant temperature it uses up energy either at its own expense or at the expense of its surroundings. This energy is called the free or available energy, to distinguish it from the quantity which we have denoted by the term U, which is the change in internal or total energy. Free energy can be denoted by A, since it is exactly equal to the *maximum* work done in *isothermal changes*.[1] The relation between the free and total energy of a system is by no means an obvious one, in fact we cannot attempt at this stage to show the relation between the two until we have discussed the second law of thermodynamics, the relation between the two being given by the expression known as the Gibbs-Helmholtz equation. The only point emphasised here is that the total or internal energy change is *not* the same thing as the free or available energy change. The use of the term "total" in regard to U must not suggest to the mind that the free energy is a fraction of this *only*. As a matter of fact, the free energy decrease (*i.e.* the maximum work output at constant temperature) in some processes actually exceeds the decrease in total energy (U) taking place in the same process, and in some extreme cases the total energy of the system may actually *increase* whilst at the same time external work is done *by* the system (*i.e.* free or available energy is given up, *e.g.* the process of vaporisation). The possibility of this arises from the fact that the change in total energy has its origin *in* the system itself, whilst the free energy, on the other hand, may be due partly to the system itself and partly or wholly to the surroundings. As a matter of fact, in the case of an isothermal gas expansion, or that of osmotic work in a dilute solution such as we have been considering, free energy which manifests itself as external work is ultimately drawn from the surroundings *entirely*, *i.e.* from the heat content of the surroundings. In processes occurring in other systems, such as liquids, the free energy may be partly drawn from the resources of the system itself as well as from the surroundings. It might be thought that there is so much vagueness about the sources of free energy that no relation could be established

[1] In an irreversible process, when *maximum* work is *not* done, there is a decrease in the free energy, and this decrease is greater than the work done. Some of the free energy has been simply lost or dissipated as heat. It is only in a reversible process that the free energy is entirely converted into external work, this work being, therefore, the maximum of which the system is capable. Further note that all this refers to changes at constant temperature only. The free energy of a system alters with temperature, whether work (maximum or otherwise) is done or not.

between it and the U of the system. We shall see later, however, that if we restrict ourselves in any system whatsoever to reversible processes, that is, to cases in which maximum work is done and, therefore, all the free energy is given out in the form of work at constant temperature, there *is* a relationship between A and U. As already mentioned, this is expressed in the Gibbs-Helmholtz equation to which we shall come later. For the sake of brevity it is customary to use the expression, "the free energy of a system," to denote the free or available energy possessed by the system and its surroundings under the given conditions. A system is said to "*possess*" free energy whether it is made to do work or not, such free energy content being measured by the maximum work the system *could* perform under the given conditions.

The Maximum Work (or Free Energy Change) involved in a (Reversible) Isothermal Process which takes place in more than one Stage.

In the cases which we have been considering, namely, the expansion of a gas or the dilution of a solution, the whole operation took place in one stage or step, *i.e.* the piston or membrane simply moved through a certain distance under given pressure relations. We now want to consider a slightly more complicated process, and we shall consider that this is also of the reversible kind, *i.e.* each stage must be so carried out as to produce *maximum* work. We shall confine our attention to the following three-stage process, as this is a very typical one which occurs again and again in the thermodynamical treatment of physical and chemical processes. Let us suppose that in a cylinder, I (Fig. 4), we have a liquid (say water) having a certain vapour pressure p_0 at a given temperature. In the second cylinder, II, we have a solution, the solvent being identical with the pure liquid in I, the solute being a non-volatile one. The vapour pressure of the solution, *i.e.* the pressure of the vapour of the solvent, is p_1 where p_1 is less than p_0, since the presence of the solute lowers the vapour pressure of the solvent. The solution in II is at the same temperature as the liquid in I. The quantity of solution in II is so great that the addition of one gram-mole of *solvent* is supposed not to have any measurable diluting effect, *i.e.* the concentration of the solute in II is supposed to remain constant. The problem before us is this:—

What is the maximum work involved in the process of transferring one gram-mole of the liquid from I and adding it to the solution in II, the temperature throughout remaining constant and the concentration of II being likewise constant? In other words, what is the maximum work done in isothermally distilling one gram-mole of liquid from I into the solution in II? In the first place, it will not do simply to place some of the pure solvent (*i.e.* the liquid in I) directly in contact with the solution in II, for this process would entail no work at all, since the solute would spread itself out into the layer of solvent against zero osmotic pressure. The same idea may be expressed by saying that

neither will it do to insert a weightless semi-permeable membrane on the surface of the solution with solvent above it, and allow this membrane to be pressed through the solvent by the osmotic pressure of the solute, as here again no work would be done, owing to the fact that no pressure resistance would be offered to the osmotic pressure. To obtain the maximum work the whole process must be carried out in a reversible manner, that is to say, in each single stage considered the difference of pressure on the sides of the piston or membrane must never be finite, *i.e.* must never exceed a value represented by dp. To carry out the whole process reversibly and thereby obtain the maximum output of work, we must consider it in three successive stages (*cf.* Fig. 4), *viz.*—

(1) One gram-mole of liquid in I is isothermally and reversibly vaporised at the pressure p_0.

(2) The gram-mole of vapour is now isolated by means of an impermeable shutter pushed in over the liquid, no work being entailed

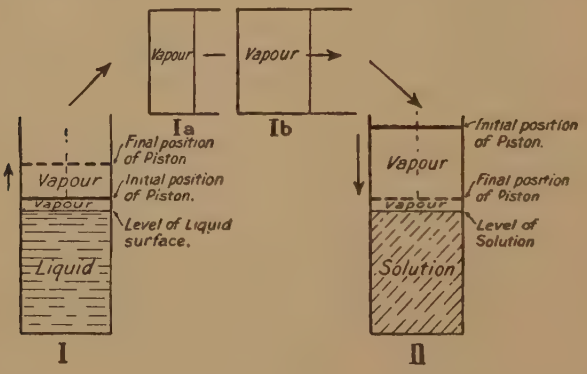


FIG. 4.

thereby. That is, we now have one gram-mole of vapour in a small cylinder I_a at pressure p_0. We suppose now that this is allowed to expand isothermally and reversibly until its pressure has fallen to $p_1 + dp$, that is, practically to p_1, the volume now being v_1, say. That is, I_a has become I_b.

(3) The cylinder I_b is brought into contact with II, and since the pressure is practically identical with that of the vapour in II, the gram-mole of vapour may be added to II reversibly. As it is pressed in at a pressure $p_1 + dp$, naturally it causes condensation of an equal mass of vapour, and if the process is carried out infinitely slowly the temperature will remain constant (heat being passed out to the surroundings). The operation of transferring one gram-mole of liquid in I to solution in II is now complete, and has been carried out reversibly. By adding together the various work terms we can obtain at once the maximum work involved in the process as a whole. The work terms are :—

In operation (1) an *amount of work p_0v_0 is done by the system* (v_0

denoting the volume of one mole of saturated vapour in I). Since the vapour remains saturated the pressure remains constant. We have neglected the molecular volume of liquid as compared to the molecular volume of vapour. In operation (2), the sliding of a frictionless, weightless shutter involves no work. That is, the act of isolating the gram-molecule of vapour in I_a involves no work, but work is involved when we allow this to expand reversibly against an opposing, continuously decreasing, external pressure which only differs from that inside the cylinder by the amount dp. Assuming the gas law for the vapour, *the work done by the vapour is—*

$$\mathrm{RT} \log \frac{v_1}{v_0}$$

The vapour is now in the state denoted by I_b. In operation (3) we have the reverse kind of process to that in operation (1). In this operation the volume of the vapour decreases, *i.e.* work is done by the surroundings upon the system, the amount being $-p_1v_1$, the negative sign denoting that there is a decrease in volume as condensation is taking place. We here neglect the increase in the volume of the solution owing to this condensation compared to v_1. These are all the work terms involved, and hence for the total process the maximum work done—

$$= \left\{\begin{matrix}\text{maximum work} \\ \text{in operation (1)}\end{matrix}\right\} + \left\{\begin{matrix}\text{maximum work} \\ \text{in operation (2)}\end{matrix}\right\} + \left\{\begin{matrix}\text{maximum work} \\ \text{in operation (3)}\end{matrix}\right.$$

That is—

$$\text{Maximum work in process} = \mathrm{A} = p_0v_0 + \mathrm{RT} \log \frac{v_1}{v_0} - p_1v_1.$$

Now it will be observed that we have assumed the vapour obeys the gas laws, since the middle term is the integral $\int_{v_0}^{v_1} p\,dv$ evaluated by putting

$$p = \frac{\mathrm{RT}}{v}.$$

If the assumption of the gas law is justifiable in regard to this term, it must be likewise justifiable in regard to the first and last terms. The first term is p_0v_0 or RT. The last term is p_1v_1 or RT, for the temperature is the same in both cases, and R is likewise the same since we have considered the same mass (one gram-mole) of vapour throughout. That is, the first and last terms cancel, and we get—

$$\text{Total maximum work in process} = \mathrm{A} = \mathrm{RT} \log \frac{v_1}{v_0}.$$

This three-stage process has therefore turned out to be identical with a single-stage one (namely, the stage I_a to I_b). This simple result is, however, only obtained by the assumption that the vapour obeys the gas laws.

Let us now consider the same process, but no longer assume the applicability of the gas law $pv = \mathrm{RT}$.

Operation (1).—The work done by the system is again p_0v_0, but this is no longer necessarily equal to RT.

Operation (2).—The work done is $\int_{v_0}^{v_1} p dv$, but we cannot write this in the form RT log $\frac{v_1}{v_0}$ since the gas law is not assumed.

Operation (3).—The work done is $- p_1 v_1$, which again is not necessarily equal to RT.

Hence the total maximum work A is given by—

$$A = p_0 v_0 + \int_{v_0}^{v_1} p dv - p_1 v_1.$$

The term $\int_{v_0}^{v_1} p dv$ may be integrated by parts whatever the relation between p and v may be. That is, we can always write—

$$\int_{v_0}^{v_1} p dv = p_1 v_1 - p_0 v_0 - \int_{p_0}^{p_1} v dp.$$

Hence—

$$A = p_0 v_0 + p_1 v_1 - p_0 v_0 - \int_{p_0}^{p_1} v dp - p_1 v_1$$

$$\text{or } A = - \int_{p_0}^{p_1} v dp.$$

This expression holds for the process involving the whole of the three stages whether the gas laws hold for the vapour or not. This is therefore the most general term for the maximum work done in a three-stage isothermal process of the type considered. If we find *as a special case* that the gas laws happen to be obeyed by the vapour in question sufficiently well, we can integrate the expression $- \int_{p_0}^{p_1} v dp$ by writing $v = \frac{RT}{p}$ which thus yields—

$$A = - RT \log \frac{p_1}{p_0} = RT \log \frac{p_0}{p_1} = RT \log \frac{v_1}{v_0}$$

as before.

It must be remembered that any *single* work term of the type considered must be the product of a pressure into an increase in volume, *i.e.* $p_0 v_0$ or $p_1 v_1$ or $p dv$ or $\int p dv$. One cannot represent a *single* work term by the product of volume into increase in pressure, say $v dp$ or $\int v dp$. It happens, however, that the three consecutive work terms involved in the process considered above do reduce down to a single $v dp$ term (owing to the operation of integration by parts), and this result, namely—

$$A = - \int_{p_0}^{p_1} v dp = \int_{p_1}^{p_0} v dp$$

is reached whether the system or substance considered obeys the gas laws or not. Although, physically speaking, we cannot represent a single work term by $v dp$, it is evident that if we are studying the special case of the work of expansion at constant temperature of a vapour or gas which obeys the gas laws, the work done $= p dv$, and this is numerically equal to $- v dp$ because the expression $d(pv) = v dp + p dv = 0$, since

pv is a constant at constant temperature by Boyle's Law. It is only, however, when $d(pv) = 0$, that is, when the gas laws are obeyed, that we can interchange pdv and vdp terms. When the system does not obey the gas laws it is necessary to find some relation between p and v which will allow us to evaluate any integrals. For vapours one may apply as a first approximation the van der Waals equation for this purpose, treating a and b as constants.

The Distinction between the Natural or Spontaneous, and therefore Irreversible, Method of carrying out a Reaction and the Thermodynamic Reversible Method of carrying out the same Reaction.

The distinction is best made clear by means of an example. Take the case of the chemical reaction which occurs between water and sulphuric acid. Let us think of an apparatus similar to that indicated in Fig. 5. In one vessel, A, there is a quantity of liquid water, and in contact with it some saturated vapour at pressure p_0. The vapour fills the space on the left-hand side of the tap C. In the vessel B there is some concentrated sulphuric acid, that is acid containing a little water, and above this acid is some vapour in equilibrium with the water in this sulphuric acid mixture. The partial pressure of the water vapour is here p', where p' is much less than p_0. This water vapour at low pressure (along with some sulphuric acid vapour which does not come into the calculation) occupies the space on the right of the tap C. If we simply open the tap, water vapour would stream from left to right, that is from the region of high pressure p_0 to that of low pressure p'. If a piston were placed in the tube it would be driven at a speed not by any means infinitely slowly, and the pressure difference on the two sides of the piston would be finite, *i.e.* $(p_0 - p')$. This process, which is the spontaneous one, is an irreversible one, since the piston is not made to move infinitely slowly with infinitely small pressure difference on the two sides.

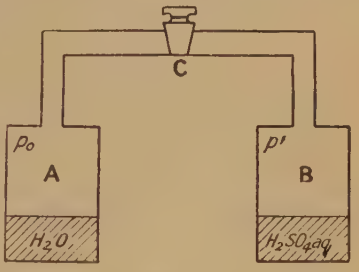


Fig. 5.

We can carry out the same transfer of water to concentrated sulphuric acid reversibly, however, by following out the three-stage work process already described. First, a certain quantity of water is vaporised by pulling out a piston infinitely slowly, the pressure on the outside of the piston being $p_0 - dp$. This vapour is now isolated and expanded, doing work against a continuously decreasing external pressure, which never differs from the actual pressure of the vapour by more than the infinitely small quantity dp. In this way the pressure of the water vapour is brought to p', or rather to $(p' + dp)$, and is then introduced

into the space over the concentrated sulphuric acid and pressed in, *i.e.* condensed infinitely slowly owing to the pressure difference on the two sides of the piston being infinitely small. The total mechanical work which is here maximum work is, as we have seen, $-\int_{p_0}^{p'} v dp$.

It will thus be clear that we can carry out the same process either in the natural or irreversible way, in which case we do *not* get a maximum output of work, or, on the other hand, we can imagine the process carried out reversibly in the thermodynamic sense, in which case we do get a definite maximum quantity of work, expressible in terms of p and v.

KIRCHHOFF'S EQUATION FOR HEAT OF REACTION (WHICH INVOLVES THE PRINCIPLE OF THE FIRST LAW OF THERMODYNAMICS).

Suppose that a system changes from a state A to a state B, *i.e.* as a particular case, let us consider a chemical reaction of any kind whatsoever in which at a temperature T, a quantity of heat Q_v is absorbed in the transformation of reactants into resultants at constant volume, then

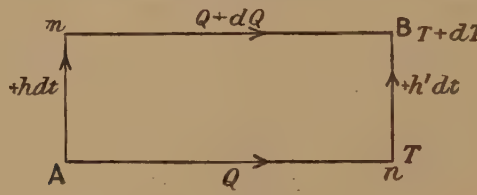


FIG. 6.

$-Q^v = U$. Suppose that the same reaction goes at a higher temperature, T + dT, then the heat which will be absorbed may be represented by $Q_v + dQ_v$. Further, let us denote by h the heat capacity of the reactants and by h' the heat capacity of the resultants. We can go from the stage A to the stage B by two independent paths, indicated in the diagram (Fig. 6.), namely, AmB and AnB. The point A denotes the system consisting entirely of the reactants and at the temperature T ; the point B denotes the system consisting entirely of resultants at temperature T + dT. By the First Law of Thermodynamics, *i.e.* by the principle of the conservation of energy, the net heat absorption or evolution via AnB must be the same as via AmB, since the system starts from the point A and ends in both cases at the point B, without any volume change, so that the heat change is identical with the internal energy change. Going via AmB we start with the reactants at A and raise their temperature to T + dT, an amount of heat + hdt being thereby absorbed (the positive sign denotes heat absorbed). Having now reached m, we suppose the reaction to take place (at T + dT) whereby the reactants are converted into resultants, the heat absorbed being $Q_v + dQ_v$. We have now reached B. Let us start again at A, and allow the reaction to go at T, the heat absorbed is Q_v. We have now

reached n. Now raise the temperature of the resultants to T + dT, the heat absorbed being + $h'dt$, we are again at B. Equating the heat effects by the two paths we obtain—

$$+ hdt + Q_v + dQ_v = Q_v + h'dt$$

or

$$\frac{dQ_v}{dt} = h' - h = h'_v - h_v$$

where the suffix v is introduced to denote constant volume;

or

$$\frac{dU}{dt} = h_v - h'_v.$$

This is Kirchhoff's equation. Its great importance lies in the fact that it allows one to calculate the temperature coefficient of heat effects from measurements of the specific heats of the substances involved in a very much more accurate manner than could possibly be done by actually measuring Q or Q_v at two different temperatures.

THE WORK DONE BY THE SURROUNDINGS (*i.e.* THE EXTERNAL AGENCY) IN COMPRESSING A GAS (*a*) ISOTHERMALLY, (*b*) ADIABATICALLY.

During the process of isothermal compression, the heat which is produced and evolved is absorbed by the surroundings which are supposed to be of so great extent that the temperature of the system remains constant, provided, of course, that the compression takes place sufficiently slowly to allow of the heat being conducted away. In an adiabatic compression, on the other hand, we suppose the gas to be isolated in a "heat-tight" case so that no heat can be added to or abstracted from the gas. If we compress this system, the temperature rises, and this rise in temperature tends to make the gas *expand*, *i.e.* the temperature effect opposes the compressing force, and hence this external agency will have to do more work upon the gas to compress it to the final volume than it had to do when the gas was being compressed isothermally—the initial and final volumes being the same in each case. If we make use of a *pv* diagram, the area represents work done, and if in the case considered the initial volume is v_1, and the final volume after compression is v_0, then work done in the *isothermal* compression can be represented by the area ABv_0v_1 (Fig. 7). The line AB is called an isothermal line. In order to indicate a greater work output, as is the case in the adiabatic compression between the two volume limits v_1 and v_0, we must trace a line such as AC, the adiabatic work being

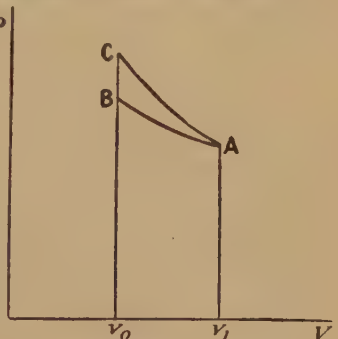


FIG. 7.

represented by the area $AC v_0 v_1$. The line AC is called an adiabatic line. On traversing AB the temperature of the gas remained constant. On traversing AC the temperature of the gas rose. *It is clear that an adiabatic line or curve is steeper than the isothermal line or curve on the* pv *diagram.* The relative position of the two lines or curves is of some importance when we come later to study thermodynamical cycles.

Thermodynamical Definition of a Perfect Gas.

An experiment carried out by Gay-Lussac, and afterwards improved by Joule, can be briefly outlined as follows (*cf.* Fig. 8). A large vessel I containing gas was connected by means of a tap to a similar vessel II, which had been evacuated. The whole was immersed in a bath, the temperature of which was measured as accurately as possible. When the tap was opened gas rushed over from I into II. There is thus an expansion of gas in vessel I, and the gas in I becomes colder because it has to compress the first portions of the gas which have gone over. At the same time the temperature in II rose because the first portions of the gas were compressed by the following portions. The temperature of the bath remained unchanged as far as Joule could observe during the whole operation. That is, the cooling effect in I must have just compensated the warming effect in II. The gas as a whole did not rise or fall in temperature on expanding into a vacuum. That is to say, on the whole no heat was either taken in or given out by the gas in the operation. Now for any process we have the three quantities U, Q, and A, connected on the basis of the First Law of Thermodynamics by the relation—

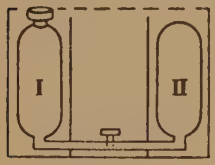


Fig. 8.

$$U = A - Q.$$

In the above operation Q = o (experimental result). Further, we see that the external work performed by the gas as a whole is zero in expanding from I to II (which was in the first place evacuated). The whole system is I + II and the volume of I + II is constant, hence no external work is done by the passage of the gas. This holds good even if there had been some gas present in II to start with, for this condition is evidently realised when passage of gas has begun. That is, A = o. Hence from the First Law it follows that U = o. That is to say that the total or internal energy of the gas has not changed. (U represents *change* in internal energy *not* internal energy itself.) We therefore arrive at the following important conclusion :—

The internal energy of a given mass of *gas* is independent of the volume occupied. As a matter of fact (as shown by the porous plug experiment, which we will consider later), any actual gas only approximates to this statement. There really was a very slight change in temperature in the bath in the Gay-Lussac-Joule experiment, though the methods employed were not sufficiently delicate to indicate it.

This slight change in temperature has been traced to the work done by the molecules in drawing themselves apart against their mutual *attractive* forces. A perfect gas from the kinetic standpoint is one in which no attractive forces exist. In the case of a *perfect* gas, therefore, there would be absolutely no change in temperature if it were to go through the process described. In other words, there would be no change in the internal energy, *i.e.* U = o. *We can thus define a perfect gas as a substance, the internal or total energy of a given mass of which is independent of the volume occupied by that mass.*

The only other factor upon which internal energy (U) depends is that of temperature. *We can thus alternatively define a perfect gas as a substance, the internal energy of which is a function of temperature only.*

It must be clearly understood that the internal energy of vapours and liquids (which physically depart far from the concept of a perfect gas) does depend upon volume as well as upon temperature. From the molecular standpoint this is due to the existence of cohesive forces (often of very great magnitude) between the molecules themselves.

It must be borne in mind, however, that the above definition of a perfect gas, though true as far as it goes, is not a complete thermodynamical definition. The complete definition will be given after we have considered the porous plug experiment of Joule and Thomson (afterwards Lord Kelvin).

Cyclical Processes or Cycles.

Reversible and Irreversible Cycles.

A cyclic process consists of a series of consecutive changes or equilibrium states through which a system may be taken, finally returning to its original position or state. The system is chemically and physically identical in all respects at the beginning and the end of the cycle; the system having returned to its original state. It is clear, therefore, that the internal energy of the system is the same before and after a cycle, for the internal energy is a physical or chemical property of the substance just as its volume or colour or shape is. That is, on completing a cycle we can say that $\pm U = o$, where $\pm U$ denotes the change in internal or total energy, and this is true for systems of any kind. The terms Q and A may, however, not be zero, for these are not chemical characteristics or properties of the system in the same sense that the internal energy is. When a system is undergoing any change, heat may be added or given out and similarly work may be done by or upon the system.

The First Law of Thermodynamics, when applied to a cycle, states that the sum of all the work terms (ΣA) *is equal to the sum of all the heat terms* (ΣQ).

This is evident, for the First Law states that for any process $U = A - Q$, and since for a completed cycle $U = o$ it follows that $A = Q$ or $\Sigma A = \Sigma Q$, when during the cycle there are several operations

involving work or heat. This holds good no matter what the system may be (solid, liquid, or gas, heterogeneous or homogeneous), and it likewise holds good whether the temperature of the system has altered at any stage of the process or not (the temperature at the final stage being, of course, equal to the initial temperature). A cycle in which the temperature does not change during any period of the operation is called an isothermal cycle. A cycle in which temperature changes do occur is called a non-isothermal cycle (the original conditions of temperature being eventually reached). A reversible cycle is one in which the various occurring processes are reversible in the sense already defined. An irreversible cycle is one in which the processes are irreversible. The First Law of Thermodynamics being an absolutely general law, embodied in the principle of the Conservation of Energy, must hold for reversible and irreversible processes and cycles alike. When we come to the Second Law of Thermodynamics we shall see that we must restrict ourselves to reversible cycles. A typical isothermal cycle might be represented as follows:—

The initial system is a vessel of liquid water and from this we remove by isothermal vaporisation at a given pressure one gram-mole. We now isolate the vapour and alter its pressure, thereby doing work against the surroundings until its pressure becomes identical with the vapour pressure of a given dilute aqueous solution contained in a second vessel at the same temperature. We now isothermally compress the gram-mole of vapour into the solution and then by means of a semi-permeable membrane remove one gram-mole of liquid. Having isolated it, transfer it to the liquid water contained in the first vessel. The gram-mole of water has now been taken round a complete cycle (which happens in this case to be an isothermal one), the initial and final states being identical. If we had carried out each single process reversibly (in the manner described in the paragraph dealing with the production of maximum work in a process involving more than one stage, and also in the treatment of maximum osmotic work production), the cycle as a whole would be called an isothermal *reversible* cycle.

Professor Orr (*Notes on Thermodynamics for the Use of Students in the Royal College of Science, Ireland*, printed privately) defines reversibility as follows:—

"A process is said to be reversible in the thermodynamic sense, if it is possible for the successive stages to occur in exactly the reverse order in point of time (all the motions, chemical changes, transference of electricity, etc., being thus reversed), *with all the mechanical forces unaltered.* (Care must be taken not to express the definition in such a way as would imply *a reversal of the forces.*)"

It must be borne in mind that a reversible process or cycle is a limiting case which we can never quite realise in practice. All naturally occurring or *spontaneous* processes are *irreversible.* We have already defined an irreversible process as one in which energy is dissipated or departs from the system permanently (though, of course, it cannot be destroyed, but must appear somewhere in space according to the prin-

ciple of the First Law). The conductance of heat from a hot system to cold without the performance of any external work is an irreversible process. That is to say, it is a matter of experience that a bar of metal if heated at one end, say, will not remain in this state of unequal temperature, but the temperature will ultimately tend to become uniform, the temperature of the bar as a whole being lower than that of the initially heated portion. Further, experience has shown that the reverse process never takes place spontaneously, *i.e.* a bar of metal at uniform temperature never of its own accord begins to rise in temperature at one end and cool at the other. The process of conductance is in fact an irreversible one. Further, motion turned into heat by friction is also an irreversible process. The reverse operation, that of a body set in motion merely by heating, never occurs. Also the process of diffusion of a gas or a solute in solution from a region of high pressure or concentration to a region of lower pressure or concentration is an irreversible process as it occurs in nature, *i.e.* the reverse process is unthinkable as a spontaneous effect. Similarly, a gas expanding into a vacuum (which is an extreme case of the foregoing process) is irreversible. Of course, it must not be forgotten that processes such as the dilution of a solution or the expansion of a gas *can* be carried out in a reversible manner, or rather we can conceive of such an operation as a limiting case under certain given conditions, *i.e.* the conditions which must be complied with to yield the maximum amount of external work. Natural or spontaneous processes never perform the maximum amount of work, and may perform no external work at all. For our purpose, however, reversible processes and cycles are the more important as the application of thermodynamics to physical and chemical problems concerns itself with these alone.

Different Forms of External Work.

So far we have considered the symbol A to refer to the work done in the expansion of a gas against an external pressure, or the work done in diluting a solution also against a pressure. *This is mechanical work.* It must not, however, be concluded that such operations as these are the only conceivable form of external work. A may also in certain cases be measured by electrical work or output of electrical energy if the system considered is capable of being set up in the form of a voltaic cell. Electrical energy is the product of electromotive force into current. It is usual to take as the unit of current the faraday, which is equivalent to 96,540 coulombs, and is the quantity of current required to deposit one gram equivalent of a metal or non-metal, *e.g.* silver or iodine. Let us consider the chemical reaction represented by the stoicheiometric equation—

$$Zn + CuSO_4aq = ZnSO_4aq + Cu$$

which may be written in terms of ions as

$$\underset{\text{(metal)}}{Zn} + Cu^{++} = Zn^{++} + \underset{\text{(metal)}}{Cu}.$$

This reaction can be made to take place in such a way as to yield electrical energy. The system is simply the Daniell cell. If E is the electromotive force, then E will also numerically represent the electrical energy connected with the deposition of one equivalent of copper in the metallic state, and simultaneously the dissolution of one equivalent of zinc from the metallic state, for the quantity of current involved in this is one faraday, and hence the electrical energy is $E \times 1 = E$. This current can do external work, such as that of driving a motor. When it is made to do maximum work the cell is acting reversibly, and we are dealing with a reversible process which experience has shown is capable of doing a considerable amount of work, although the volume remains practically constant.

Another form which A may take is work done against gravity. Thus let us take the surface layer of a liquid as our system. This possesses free or available capillary energy which manifests itself by the phenomena of surface tension. The free surface energy in this case can be measured by making it do work against gravity by drawing a column of liquid up a narrow tube. If h is the height of the column when the meniscus becomes steady, ρ the density, and g the acceleration of gravity, the external work done by the surface energy is $(h\rho \,.\, g)$ work units. Free energy therefore can manifest itself in all types of external work. If the temperature is kept constant and the work be maximum work, then, no matter what the nature of the external work may be, it gives quantitatively the decrease in free energy of the system and its surroundings.

Before passing on to the consideration of the Second Law of Thermodynamics it may be well to state once more the First Law, *viz.* : IF OR WHENEVER *heat is converted into work of any kind, or work into heat, there is always a definite quantitative relationship between the heat which has disappeared as such and the work which has been done, or* vice versâ.

THE SECOND LAW OF THERMODYNAMICS.

It will be noticed that in the definition of the First Law given above, stress has been laid on the words "*if* or *whenever*" heat is converted, etc. Experience has shown that work is always capable of being transformed into heat, but this is not always the case for the opposite transformation, that of heat into work. Thus whilst the Law of the Conservation of Energy furnishes us with the relationships which must necessarily hold when one form of energy is transformed into another, the so-called Second Law brings out a peculiarity which belongs alone to energy in the form of heat as regards its convertibility into other forms of energy. The Second Law as a statement of the results of experience teaches us that there are certain definite limitations in connection with the transformation of heat into other forms of energy. Qualitatively one may state it thus :—

External work, such as the kinetic energy of moving bodies, may be

transferred in many ways, and *completely* into another form, heat for example; but conversely the reconversion of heat into work is not a complete one, and may not even be possible to the slightest extent. Remember this does not in any way contradict the First Law. For whether the heat transformed be small or great the First Law holds absolutely, in that this small or great heat change is transformed quantitatively into some equivalent form of energy, say motion. The First Law simply states that if or whenever heat is transformed an equivalent of some other energy appears. It does not state that heat under all conditions *can* be transformed. The distinction is most important. As an example of heat that no one has been able to utilise, *i.e.* transform, we might take the heat energy of the ocean. We know that the ocean is at a certain temperature, and that it requires energy to be added to it to raise its temperature. Hence it must contain energy in the bound state. No one has by any device been able to use the heat energy, say to drive the screw of a vessel in the ocean itself. There are numerous other instances, and we have gradually come to the conclusion that for some reason or other we cannot *always* convert heat into work. This naturally leads to the question: What is the condition which determines this conversion or non-conversion of heat into work? The answer is simple, it is a question of temperature or rather temperature differences. We cannot convert heat into work unless we allow this heat to pass from a high temperature to a lower one. The efficiency of the process, *i.e.* the fraction of heat converted into work, is dependent on the temperature difference between the hottest and coldest part of the system. This is why the heat of the ocean is unavailable; we ourselves are living at the same temperature (or even higher). The ship, for example, is at the same temperature as the ocean, and hence, if the above principle is correct, one cannot expect the heat of the ocean to be utilisable by the ship. On the other hand, the inhabitants of a colder planet might readily utilise our ocean heat, and, indeed, the heat of our planet itself, for work, if only the mechanical difficulties could be overcome.

The Second Law, as stated by Clausius, is as follows:—

"It is impossible for a self-acting machine working in a cycle, unaided by any external agency, to convey heat from a body at a low temperature to one at a higher temperature; or heat cannot *of itself* (*i.e.* without the performance of work by some external agency) pass from a cold to a less cold body."

First note the phrase "of itself"—heat cannot of itself pass from a low to a high temperature. We have seen that by means of an adiabatic compression of a system the temperature rises, heat being evidently thereby carried up the temperature scale. But this does not contradict the above statement about the *natural* flow of heat, for we have, by the aid of external agency, had to do work, namely, to compress the system in order to make the temperature rise. It is a known experimental fact that systems, say gases, naturally tend to expand, the molecules tend to fly apart and not to contract. This fact is evidence, of a molecular

kind, for the Second Law, for by expanding the system cools. So much for the qualitative statement of experience. We now come to the question of a quantitative statement. It must be clearly understood that the quantitative formulation of the Second Law (which will be given in a moment) holds only *for a reversible cycle* of changes. We have already discussed changes of this nature. One other instance may be given. Suppose a system of any kind—an engine, as it is called—takes in heat Q_1 from the boiler at temperature T_1 and drives a piston and crank, thereby doing external work, and then gives out heat Q_2 to the condenser at temperature T_2, the amount of heat given out to perform work is $Q_1 - Q_2$ and this will be quantitatively the work done; for friction is entirely absent, as we suppose it to be an ideal engine. If, now, some external agency performs a quantity of work on this engine numerically equivalent to $Q_1 - Q_2$, and if the engine thereby takes in heat Q_2 at T_2 and gives up Q_1 at the high temperature T_1, then the engine is a reversible one. When the engine is working directly it must be doing maximum work, *i.e.* just able to overcome opposing forces in order to comply with the condition of working reversibly.

The efficiency of any engine is—

$$\frac{\text{work done}}{\text{heat taken in from boiler at } T_1}.$$

It is identical with $$\frac{Q_1 - Q_2}{Q_1}.$$

Now there is a theorem called Carnot's Theorem, the validity of which depends on the trustworthiness of the Second Law. This theorem states that a reversible engine has the maximum efficiency, and further, that the efficiency of all reversible engines *working between the same temperature* limits is the same. This holds good whatever the nature of the substance doing work.[1] It can be shown that the efficiency of a reversible engine is connected with the temperature limits referred to by the expression—

$$\eta = \frac{T_1 - T_2}{T_1}.$$

So that we may write $$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

If we take the case in which the highest temperature of the engine or system is T and the difference between this temperature and the coldest temperature is dT, then the amount of heat converted into work is dQ instead of $Q_1 - Q_2$ and the above relation takes the form—

$$\frac{dQ}{Q} = \frac{dT}{T}.$$

But, according to the First Law, the heat dQ which has been converted into work may be put identical with an external work quantity dA if there has been no loss by friction, and if in fact dA represents the

[1] This is discussed in a more advanced treatment given later.

maximum amount of work dynamically equivalent to dQ,[1] the above relation takes the form—

$$dA = Q\frac{dT}{T}$$

for all substances traversing a reversible cycle. In words, the term dA represents the maximum amount of work which can be obtained from an engine working between the temperature limits T and T − dT, the heat taken at the high temperature T being Q. This may be taken as the quantitative statement of the Second Law. If the engine is not a reversible one it will in general do less work (according to Carnot, it can never do more), and in such a case we can only write the inequality—

$$dA < Q\frac{dT}{T}.$$

As before mentioned, we shall confine our attention to reversible processes only.

Deduction of the Expression $dA = Q\frac{dT}{T}$ for the Case of a Perfect Gas.

We have briefly indicated how the above relation is obtained in general for any system undergoing a reversible cycle of changes. It will be more easily grasped, perhaps, if we now obtain again the same expression for the concrete case of a perfect gas engine. Let us suppose the gas is enclosed in a cylinder fitted with a weightless, frictionless piston. Suppose we are dealing with one mole whose volume is v_1 at temperature T. Let the gas expand isothermally from v_1 to the volume v_2. The maximum work which could be done by the gas in such an isothermal change is—

$$A = RT \log \frac{v_2}{v_1}.$$

Now by the First Law—

$$U = A - Q$$

but we have kept the temperature constant, and hence, since U (which is *change* in internal energy) depends only on temperature and is independent of volume for a perfect gas (as we have already seen), it follows that, in the present case—

$$U = 0 \text{ and therefore } A = Q$$

i.e.

$$A = Q = RT \log \frac{v_2}{v_1} \quad . \quad . \quad . \quad . \quad (1)$$

or

$$\frac{Q}{T} = R \log \frac{v_2}{v_1},$$

Q (with a + sign) denotes the heat taken in from the reservoir while the work was being done at constant temperature.

[1] 1 calorie = 4·2 joules = 4·2 × 10^7 ergs.

This important formula[1] does not by any means say that the work A *must* always be done when a gas expands isothermally from the smaller volume v_1 to the larger volume v_2. We have only need to call the Gay-Lussac or Joule experiment to mind (namely, the expansion of a gas into a vacuum) in order to see that the term A can be equal to zero. Every possible value of A between zero and $RT \log \frac{v_2}{v_1}$ is not only conceivable but is also attainable. The value $RT \log \frac{v_2}{v_1}$ is, however, a maximum one. If we try to bring the gas back isothermally from the greater volume v_2 to the initial volume v_1 we need to expend more or less work depending upon the efficiency of our compressing machine. But, here again, if the efficiency of the engine (the gas) is a *maximum*, the minimum work which the compressing machine has to do to bring the gas back to its original state is at least A. The maximum production of work by the perfect gas engine is therefore that which accompanies a process taking place reversibly.

Now let us consider the gas as carrying out the same operation at a lower temperature $T - dT$, the same mass of gas working between the same volume limits v_1 and v_2 as before. The *maximum* work done by the system is now—

$$(A - dA) = R(T - dT) \log \frac{v_2}{v_1} \text{ per mole} \quad . \quad . \quad (2)$$

Note particularly that *the volume limits are the same* even though we have considered the two cases at different temperatures. There is no volume change due to temperature assumed or involved in the above considerations.

If we now subtract equation (2) from equation (1) we obtain—

$$dA = R\,dT \log \frac{v_2}{v_1},$$

but

$$R \log \frac{v_2}{v_1} = \frac{Q}{T},$$

$$\therefore dA = Q\frac{dT}{T}$$

which is the expression we have sought.

This expression can now be slightly transformed into—

$$T\left(\frac{dA}{dT}\right)_v = Q.$$

The differential on the left-hand side is a partial one. The expression stands for the change in the maximum work which takes place when the process is carried out, first at one temperature and then at a temperature 1 degree lower. The work has been carried out between the same volume limits at each temperature, *i.e.* a change in temperature does *not* involve a change in volume although it does involve, of course,

[1] Haber, *Thermodynamics of Technical Gas Reactions*, English Edition, p. 18.

a change in maximum work, for the pressure is different in the two cases. The restriction in regard to working between the same volume limits in the work process at the different temperatures, which is self-evident in the particular case of the gas, is a general restriction, whatever the working substance may be.

The Gibbs-Helmholtz Equation.

The First Law states that—

$$U = A - Q.$$

From the Second Law one can deduce for a reversible cycle—

$$Q = T\left(\frac{dA}{dT}\right)_v$$

and hence both combined for a reversible cycle give—

$$A - U = T\left(\frac{dA}{dT}\right)_v.$$

This is known as the Gibbs-Helmholtz equation and is the most important thermodynamical equation from the standpoint of the application of thermodynamics to chemical problems. It gives the true quantitative relation between the change in internal energy U and the change in free energy A which occur during any given *reversible* process. If the process is of such a nature that the free energy does not alter with temperature, or only very slightly, the term $\frac{\partial A}{\partial T}$ will be zero, or practically so. In such a case A = U, *i.e.* the free energy becomes identical with the change in internal energy. This happens to be nearly true in the case of the chemical reaction occurring in the Daniell cell, but it must only be regarded as being of an accidental character. In *general* A and U are not numerically identical, the quantitative relation between them being given by the Gibbs-Helmholtz equation.

The equation referred to may be slightly modified as follows. We have seen, in dealing with the expression for the First Law, namely—

$$U = A - Q$$

that we can also write this in the form—

$$-Q_v = A - Q$$

where $-Q_v$ represents the heat evolved when the process occurs without alteration in volume, this being identical with the decrease in internal energy U. Substituting $-Q_v$ for U in the Gibbs-Helmholtz equation, we get—

$$A + Q_v = T\left(\frac{\partial A}{\partial T}\right)_v.$$

Application of the Expression $dA = Q\frac{dT}{T}$ to some Reversible Cycles. The Carnot Cycle.

First let us consider an isothermal reversible cycle. In this case $dT = 0$, and therefore $dA = 0$. Hence we conclude that in a completed reversible isothermal cycle the sum of all the work terms done by or on the system cancel one another and equate to zero. This conclusion is of great importance, and receives frequent application.

Let us next consider a particular type of a non-isothermal reversible cycle consisting of an isothermal expansion of a system (solid, liquid, or gas), followed by an adiabatic expansion, this in turn being followed by an isothermal compression, and this by an adiabatic compression, thereby bringing the system back to its original state. Such a cycle, consisting of two isothermal volume changes and two adiabatic volume changes, is called a Carnot Cycle. Let us suppose, for the sake of the mental picture, that the substance is a gas. We shall not, however, assume any gas laws in the first instance, and hence the general result will be valid for any system. Suppose the initial state is represented on the *pv* diagram (Fig. 9) by the point A.

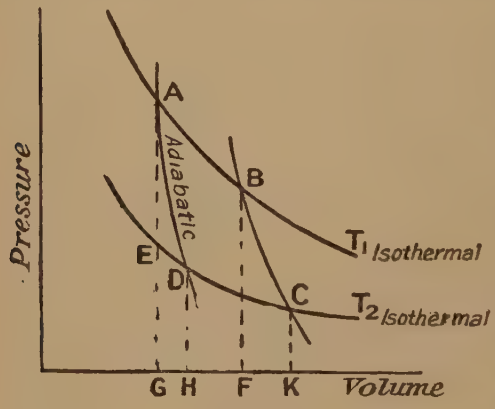


Fig. 9.

First Step.—Suppose the system expands through an infinitely small volume *dv* isothermally and reversibly, the work done (*i.e.* maximum work) is represented by the area ABFG. During this expansion it has taken in a quantity of heat Q from the reservoir. This heat can evidently be expressed also by the term $\left(\frac{\partial Q}{\partial V}\right)_T dv$, the partial differential ∂Q denoting the heat which has to be taken in to keep the temperature constant while the volume increases by unity.[1]

[1] The symbol $\frac{dx}{dy}$ denotes the change of x with y, other variables such as z simultaneously changing. The symbol $\frac{\partial x}{\partial y}$ denotes the change of x with y, all the other variables (such as z) being kept constant. The expression $\frac{\partial x}{\partial y}$ is a partial differential. To indicate more clearly the variable (z) which is kept constant during the change of x with y, the partial differential can be written $\left(\frac{\partial x}{\partial y}\right)_z$.

Second Step.—The system expands adiabatically (no heat entering or leaving) and the temperature falls by dT. The system is now at the point C. During the second step the system does work represented by area BCKF.

Third Step.—The system, now at the lower temperature, is isothermally and reversibly compressed, the work done upon it being represented by the area below CD, *viz.*: C_1D_1HK. It gives out a quantity of heat at this lower temperature, which is a little less than Q.

Fourth Step.—The system is further adiabatically compressed, the temperature rising until the point A is once more reached. The work done upon the system in this step is represented by the area ADHG.

The cycle is now complete, and the *net work* done by the system is the area ABCD. This area is also the product of AE into FG. Now AE is the increase in pressure experienced by the system when it is kept at constant volume, and its temperature is raised by dT. We can express this analytically by saying that—

$$\text{AE} = \left(\frac{\partial p}{\partial \text{T}}\right)_v d\text{T}.$$

Further, the line FG corresponds to a small volume change dv, so that the net work done by the system, namely dA, can be expressed—

$$d\text{A} = \left(\frac{\partial p}{\partial \text{T}}\right)_v d\text{T} \times dv.$$

Now let us apply the relation deduced from the Second Law for a reversible cycle, *viz.*—

$$d\text{A} = \text{Q}\frac{d\text{T}}{\text{T}}.$$

Q is the heat taken in at the higher temperature, and we have seen that this is, in this case, $\left(\frac{\partial \text{Q}}{\partial \text{V}}\right)_\tau dv$. Hence the above expression may be written—

$$\left(\frac{\partial p}{\partial \text{T}}\right)_v d\text{T} \times dv = \left(\frac{\partial \text{Q}}{\partial \text{V}}\right)_\tau dv \times \frac{d\text{T}}{\text{T}}$$

or

$$\left(\frac{\partial p}{\partial \text{T}}\right)_v = \frac{1}{\text{T}}\left(\frac{\partial \text{Q}}{\partial \text{V}}\right)_\tau.$$

This holds for any system, gaseous, liquid, or solid, homogeneous or heterogeneous.

The meaning of $\left(\frac{\partial \text{Q}}{\partial \text{V}}\right)_\tau$ is the heat which has to be added to a system which is increasing by 1 cubic centimetre in order to keep the temperature constant. It is therefore the latent heat of expansion of the system and may be denoted by l. Hence—

$$l = \text{T}\left(\frac{\partial p}{\partial \text{T}}\right)_v.$$

Remember, this latent heat of expansion may refer to a homogeneous phase (completely gaseous, completely liquid, or completely solid). It may also refer to those cases of change of state in which the term "latent heat" is more familiar.

The Clapeyron Equation.

Let us apply the relation—

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial Q}{\partial V}\right)_T = \frac{l}{T}$$

to the case of a change of state from liquid to vapour. If λ is the ordinary latent heat per gram of the substance, it is clear that if v_1 is the specific volume of the liquid, *i.e.* the volume of 1 gram, and v_2 is the specific volume of the vapour, then λ refers to an increase in volume of $v_2 - v_1$. Hence the latent heat per unit volume-increase, *viz.* l, is given by $\frac{\lambda}{v_2 - v_1}$. Hence the above expression becomes—

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{\lambda}{T(v_2 - v_1)}$$

$\left(\frac{\partial p}{\partial T}\right)_v$ represents the change in vapour pressure of the liquid per degree rise in temperature. Since, however, we know that the pressure of saturated vapour is independent of the volume of the vapour so long as any liquid is present, we need not retain the restriction of constant v in this case, but may simply write—

$$\frac{dp}{dT} = \frac{\lambda}{T(v_2 - v_1)}.$$

This is known as the Clapeyron equation. It allows one to calculate, for example, the latent heat of vaporisation at a given temperature if we know the vapour pressure-temperature curve, and the specific volumes of liquid and vapour respectively. Note that up to this point we have not assumed that the vapour obeys the gas laws, or, indeed, any law. The expression may, however, be made more amenable to calculation, and may still be regarded as accurate for all ordinary purposes if such an assumption be now made. Further, let us neglect the volume of the liquid v_1 compared with that of the vapour v_2, which is quite justifiable as long as we are at temperatures considerably below the critical point (at which point $v_1 = v_2$). According to the gas equation $v_2 = \frac{RT}{p}$, and hence the Clapeyron equation becomes:—

$$\frac{dp}{dT} = \frac{\lambda p}{RT^2}$$

or

$$\frac{1}{p}\frac{dp}{dT} = \frac{\lambda}{RT^2}$$

or

$$\frac{d \log p}{dT} = \frac{\lambda}{RT^2}.$$

If we consider 1 mole as the unit of mass, then λ will be the molecular heat of vaporisation, and R will be approximately 2 calories.

1. *First Illustration.*—At what height must the barometer stand in order that water may boil at 101° C.? Let the rise be x cms. of mercury for 1° rise in boiling point of water. That is—

$$\frac{\partial p}{\partial T} = x \text{ cms.} = x \times 13{\cdot}6 \times 981 \text{ (dynes per degree)}$$

$$p = 1 \text{ atmosphere} = 10^6 \text{ dynes approximately.}$$

Hence
$$\frac{1}{p} \cdot \frac{dp}{dT} = \frac{x \times 13{\cdot}6 \times 981}{10^6}.$$

Now $\lambda = 536$ calories per gram. R = 2 calories per mole, which equals $\frac{2}{18}$ calories per gram.

$$\therefore \frac{x \times 13{\cdot}6 \times 981}{10^6} = \frac{536 \times 18}{2 \times 373}. \quad \therefore \quad x = 2{\cdot}7 \text{ cms.}$$

Hence the barometer must be 787 mms.

2. *Second Illustration.*—What will be the change in freezing point of water if the pressure on the water be increased by 1 atmosphere?

We can apply the thermodynamic relation of Clapeyron in its accurate form, *viz.* $\frac{dp}{dT} = \frac{\lambda}{T(v_2 - v_1)}$, to the phenomenon of fusion.

The specific volume of liquid water (*viz.* v_2) is 1 c.c. The specific volume of ice (*viz.* v_1) is 1·1 c.c. approx. Hence $v_2 - v_1 = -0{\cdot}1$ c.c. (note the minus sign). λ here denotes the latent heat of fusion of ice, which is 80 calories per gram, or $80 \times 4{\cdot}2 \times 10^7$ ergs per gram.

Now
$$\lambda = T(v_2 - v_1)\frac{dp}{dt}.$$

That is
$$80 \times 4{\cdot}2 \times 10^7 = 273 \times (-0{\cdot}1) \times \frac{dp}{dt}$$

or
$$\frac{dp}{dt} = -1{\cdot}2 \times 10^8.$$

The minus sign shows that by putting on positive pressure *the temperature of fusion falls*, this being due, as we have seen from the above, to the fact that the specific volume of water *is less* than the specific volume of ice. The term $1{\cdot}2 \times 10^8$ represents the pressure in dynes—for all the quantities have been given in C.G.S. units—required to lower the freezing point 1°.

The reciprocal of this, *viz.*

$$\left(-\frac{dt}{dp}\right) \text{ or } \frac{1}{1{\cdot}2 \times 10^8} \text{ or } 0{\cdot}83 \times 10^{-8},$$

is the lowering of freezing point (in degrees) due to increasing the pressure 1 dyne. Since 1 atmosphere is 10^6 dynes, the lowering of freezing point due to an increase of 1 atmosphere will be $0{\cdot}83 \times 10^{-8} \times 10^6$, or 0·0083°. So that if the pressure on freezing water be raised

from 1 atmosphere to 2 atmospheres, the freezing point will be $-0{\cdot}0083^\circ$ C. It will be seen how extremely small the effect of pressure is on the freezing point, *i.e.* on fusion, this being traced to the small volume changes which occur on fusion; on the other hand, large volume changes occur on vaporisation, and therefore the effect of pressure changes on the boiling point are, of course, great. The above considerations on the fusion point afford an obvious explanation of the phenomena known as the *regelation of ice*. In this experiment a wire is hung over a block of ice, the wire being weighted. It is found that the wire cuts its way through the ice, which, however, freezes behind it so that the block remains as a whole. The effect of the wire is to cause a local increase in pressure on the ice. This causes the ice to melt in the absence of an artificial lowering of the temperature, because as we have seen increase of pressure lowers the freezing point, *i.e.* the equilibrium temperature at which ice and liquid co-exist. The wire sinks in the water thus formed. This water and also the adjacent portion of the ice is at a temperature below 0° C, owing to the absorption of heat which has become latent in the act of melting the ice. Hence when the supercooled water is no longer subject to the extra pressure produced by the wire it freezes again, leaving the block, as a whole, intact. It is clear, as already pointed out, that this phenomenon of regelation is really dependent on the fact that $\frac{dp}{dt}$ is a negative quantity, and this is dependent on the fact that the specific volume of ice is greater than that of liquid water. In the case of sulphur, for example, when it reaches the temperature (the transition temperature) at which the rhombic passes into the monoclinic form, or the monoclinic into the liquid, it is found that the specific volume of the phase which is more stable at the lower temperature, is *less* than the specific volume of the phase which is more stable at higher temperatures, and hence $\frac{dp}{dt}$ is positive, and so an increase of pressure would raise the transition or melting point. No regelation phenomena could possibly occur in such a case.

From these few illustrations it is evident that the Clapeyron equation is one of the most fundamentally important thermodynamic relations in the study of chemical and physico-chemical problems.

Dependence of Vapour Pressure Upon External Pressure.

If we have a system consisting of liquid and saturated vapour in a cylinder, we have stated that the system will be in equilibrium if the pressure put on the piston at the top of the cylinder is p_0, where p_0 is the pressure of the saturated vapour. This is how the equilibrium is usually regarded. It must not be forgotten, however, that all experiments are carried out in a gravitational field of force, and hence a column of vapour exerts a hydrostatic pressure downwards just as a column of liquid would do. In fact, the pressure exerted by the vapour at the

foot of the column is slightly greater than that exerted by it at the top by an amount which represents the hydrostatic pressure of the column of fluid. In a sense, therefore, the vapour acts as its own external pressure thereby altering to a minute extent the value of the pressure which the saturated vapour would possess were it entirely free from gravitation. We may conceive of this effect as greatly magnified by the following device. Let us imagine that we can pump in an inert gas (*i.e.* one which does not react either with the vapour or the liquid). The total pressure exerted by the system is now considerably greater than before. Suppose that the balancing external pressure is P. This is equal to the partial pressure of the saturated vapour plus the pressure exerted by the inert gas. We cannot assume, however, that the partial pressure of the vapour retains its old value p_0. As a matter of fact it possesses a new value p which is greater than p_0. By means of the inert gas therefore, it is possible to alter the value of the saturated vapour pressure. The connection between the change so produced in the pressure exerted by the vapour and the external pressure P is given by the relation

$$dp/d\mathrm{P} = v/\mathrm{V}$$

where v is the specific or molecular volume of the liquid, and V is the specific or molecular volume of the vapour under the same pressure.

That the alteration in the vapour pressure is a small quantity is at once shown by the ratio v/V. Thus in the case of water at 100° C., the molecular volume of the liquid may be taken to be 18 c.c. approximately, and the molecular volume of the vapour as 20,000 c.c. approximately. Hence $v/\mathrm{V} = 0{\cdot}0009$ approximately. This small fraction denotes the increase in the saturated vapour pressure expressed in atmospheres, due to increasing the external pressure by one atmosphere. The change is of the order of one part in 1000 and is therefore a negligible quantity. It follows, however, that in vapour pressure measurements the static method gives the true value whilst the dynamic or streaming method gives the vapour pressure at an external pressure of one atmosphere. The difference between the two values is, however, often undetectable.

The above expression will be deduced later, first by a very simple method and then by a more exact method due to Porter (cf. chap. IX.). It will there be observed that the v and V terms must be defined with precision in respect of the pressure under which each is supposed to be measured.

CHAPTER II.

Further Consideration of Thermodynamical Principles.

According to the First Law, as we have already seen, whenever mechanical energy is converted into heat or heat into mechanical energy, there is a constant ratio between the two. In a given expenditure of one sort of energy we find an "equivalent" of some other form of energy. Taking 1 calorie as the unit of heat energy, it has been shown that this is equivalent to 4·189 joules or $4{\cdot}189 \times 10^7$ ergs (mechanical energy units).

Instead of making use of the terms Q, U, and A to denote *changes* in the heat effect, internal energy, and external work respectively, we shall simply use the above terms to denote heat, internal energy, and external work in general; while to denote changes in any of these quantities we shall apply the more mathematically accurate form of notation, that of the differential calculus. Thus the First Law of Thermodynamics may be stated in the form of the equation—

$$dQ = dU + dA$$

which is the same thing as saying, that when one adds a small quantity of heat dQ to a system, there results thereby, a small increase dU in the internal energy of the system, and at the same time the system does a small quantity dA of external work. Naturally these must be all expressed in the same units—ergs, joules, or calories—in order that the two sides of the equation may be numerically identical.

The Form of A or dA.

Any "work term," say dA, is always made up of two factors, as we have seen. Energy expended or work done (by a body) can always be expressed as the product of a capacity factor into an intensity factor.

(1) In the case of a very small expansion of a system by an amount dv against a pressure p, the work—

$$dA = p\,dv$$

p being the intensity factor, v the capacity factor.

(2) Suppose a system, such as a stretched string, is being elongated by a tension T, then if the change in length is dl the work done *on* the system is $T\,dl$, or the work done by the system is $-T\,dl$. In this case T is the intensity factor, l the capacity factor.

Form of dU.

It is also reasonable to assume that part of dU might be regarded as expressible in terms of factors. But the idea conveyed by internal energy is a very composite one, being more composite in the case of solids and liquids than in the case of gases, and being likewise influenced by the molecular or atomic complexity of the system. It is impossible to state numerically in any energy units what the absolute value of U[1] is for a given body. We can only measure differences in U, namely, dU, in certain cases consequent upon changes in any of the factors, such as temperature or pressure, which define the state of a system.

Variables of a System.—Complete and Incomplete Differentials.

The most familiar case in which we have two variables, p and v, both depending on each other, and also on a third, which we shall call T, is the expression for the behaviour of a perfect gas, namely, $pv = RT$. If we consider a plane diagram in which p is plotted against v, the quantity T being kept constant, we obtain the familiar hyperbolic curve stretching between any two chosen points, a, b (Fig. 10). Any one of the three variables p, v, T, can be treated as a function of the other two, *i.e.* T is a function of p and v, or p is a function of v and T, or v is a function of p and T. These cross connections are represented for the particular case of a perfect gas by the equation already given. For a perfect gas, therefore, if it be taken through a series of changes—expansions, compressions, heating, cooling—and again brought back to its original state, that is, if we bring back the pressure and volume to the original values p_0 and v_0, the temperature will also have been found to have come back to its original value T_0. In such a case a small change in temperature, which is denoted by dt, is said to be a complete differential, because the value of T at any stage is completely determined by the values of p and v at that stage. Suppose, however, that in the cycle of changes through which we put the gas there is external work done, then on completing the cycle it will be found in general that the system has either done a nett amount of work, or has had a nett amount

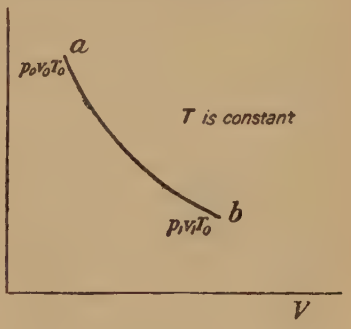


Fig. 10.

[1] Perhaps it should be again emphasised that the significance of U in this chapter and in the succeeding one, in which we deal with the continuity of state, is not the same as in the preceding chapter. The " U " of the preceding chapter is here represented by $-dU$.

of work done upon it. If either happens, dA cannot be regarded as a complete differential, because on coming back to its original state the system has suffered either a permanent gain or loss of work. (In the single case of a perfect gas going through a cycle of operations at constant temperature dA = o on the whole cycle.) The difference between the two cases, namely, complete and incomplete differentials, as exemplified by dT and dA respectively, lies in this: that the value of dT depends only on the position, say the point a, in the path of transformation. Whereas dA depends on the path itself. Thus if we go from a to b along the path indicated in the diagram, and then return along the same path from b to a, dA is certainly nothing. But if we return from b to a by a different path—say one lower down on the diagram—and finally reach a, the total work or $\int d$A is not zero. $\int d$T is zero no matter what path we follow. A, it must be remembered, means external work done by or on the body. The term U denotes internal energy contained in the body. This quantity U is considered to be simply dependent on the state of the substance—gas, liquid, or solid—at any given stage. It is considered independent of the path by which the stage was reached. It therefore corresponds to the behaviour of T in the case of a perfect gas; dU is therefore a complete differential. On taking a body round a cycle of changes and bringing it back to the original point, the value of U will once more be U_0, although, of course, at different points during the cycle it possessed values sometimes greater, sometimes less, than this. One might look then upon the U of a body as something analogous to an inherent physical (or chemical) property of the body. [The property of boiling point is always characteristic of a substance when the pressure is brought back to atmospheric, no matter what has happened to the substance between two boiling point determinations, provided, of course, it has not been exposed to conditions so extreme as to decompose it.] One must be quite clear therefore as to the distinction between internal energy changes (or total energy changes, as they are sometimes called) and external work terms (or free energy changes as they are sometimes called). The expression dU is a complete differential, the change in U being completely determined by the initial and final states; dA, on the other hand, is an incomplete differential, the change in A being dependent on the path whereby the transformation from the initial to the final state of the system was made. In any change from the point a to point b, knowing the first and last states, we know dU, and therefore we know (dQ − dA), but we do not know either of these quantities separately, unless one knows the history of the change. For the given increase in energy dU we cannot tell how much of this energy was given to the body in the form of heat + dQ, and how much was given in the form of work done (− dA)[1] upon it (this latter being transformed into internal energy).

Now let us consider the heat term Q. As already stated in the

[1] We reckon as a convention simply work done by the system as +, work done upon it as −.

preceding chapter on Elementary Thermodynamics, strictly speaking, we cannot use the term heat *in* a body. One can pass heat into a body, but it is no longer heat when it gets in. Take, by way of illustration, the passage of heat into a body which is expanding at constant temperature. The heat has simply gone to do external work, and if it is converted it is no longer "heat". Heat enters a system but immediately becomes something which is not heat. In general, there is an increase in the internal energy of the system and also some external work is done. In fact, we have the relation $dQ = dU + dA$. Hence, if a piece of matter be put through a cycle of changes and comes back to its original state, the internal energy U is the same as at the beginning, just as the matter itself is the same. That is, the sum of all the change in U, namely, ΣdU, is zero for the complete cycle. The sum of all the work terms done by or on the system, namely ΣdA, is however, not zero, and, THEREFORE, from the above equation $dQ = dU + dA$, the term dQ or ΣdQ (if there has been more than one heat addition or subtraction on completing the cycle) is not zero. Hence, we cannot speak of heat *in* a body in the same sense as we speak of internal energy (U) in a body. Functions or quantities which come back to their initial values when the cycle is completed and the original conditions (say, of pressure and temperature) once more obtain are called *complete differentials*, and we can express the fact mathematically in the case of a quantity x by the equation—

$$\int dx = 0$$

for a completed cycle, in which we have once more arrived at the starting point. By way of illustration, since we have already seen that internal energy change is a complete differential, we can write—

$$\int dU = 0$$

for a completed cycle. But $\int dA \neq 0$ being an incomplete differential, and since in the case of a completed cycle $\int dU = 0$, it follows that $\int dQ = \int dA$, the conclusion being that $\int dQ \neq 0$, *i.e.* dQ is an incomplete differential.

PROPERTY OF THE COMPLETE DIFFERENTIAL.

If there are two quantities x and y upon which a third quantity W depends, we can express the fact by the relation—

$$W = f(x, y).$$

Suppose x and y plotted as co-ordinates in a rectangular system (see Fig. 11).

Let the initial state of W be represented by the point A and let its final state in a transformation be represented by the point C. We can pass from A to C by different paths. Consider two such paths, *viz.* one *via* B, the other *via* D.

1*st Case.*—Passing horizontally from A to B means simply that x has altered by an amount dx while y has remained constant. Passing

from B to C means that y alters by an amount dy while x remains constant. The initial value of W at A may be called W_0, and when it reaches B it has evidently the value—

$$\left(W_0 + \frac{\partial W}{\partial x}dx\right).$$

When C is reached the value of W is—

$$\left(W_0 + \frac{\partial W}{\partial x}dx\right) + \frac{\partial}{\partial y}\left(W_0 + \frac{\partial W}{\partial x}dx\right)dy \quad . \quad . \quad (1)$$

2nd Case.—Passing vertically from A to D means that y has altered by an amount dy while x has remained constant. Passing from D to C means that y remains constant while x changes by the amount dx. The initial value of W at A is as before W_0. On reaching D it has the value $\left(W_0 + \frac{\partial W}{\partial y}dy\right)$.

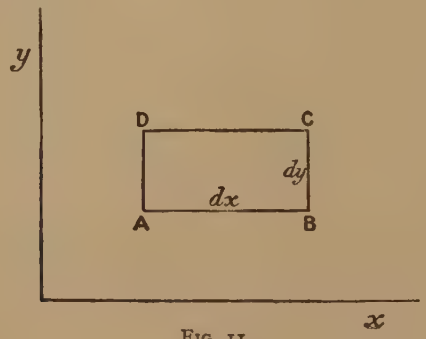


FIG. 11.

When C is reached W has the value—

$$\left(W_0 + \frac{\partial W}{\partial y}dy\right) + \frac{\partial}{\partial x}\left(W_0 + \frac{\partial W}{\partial y}dy\right)dx \quad . \quad . \quad (2)$$

If W depends only on the two variables x and y, that is, if W is completely determined by the instantaneous values which these two variables possess at any moment, it is evident that on going round any cycle on the x, y diagram and returning to A, $\int dW$ will be zero, *i.e.* dW is a complete differential. Hence, it does not matter what path is followed in going from A to C, the value of W at C will be the same in each case. That is, expression (1) is equal to expression (2), or,

$$\frac{\partial}{\partial x}\left(\frac{\partial W}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial W}{\partial x}\right).$$

Remember this relationship, which we shall apply in many instances later, only holds good if dW is a complete differential. If this is not the case, the equality between expressions (1) and (2) will not neces-

sarily be true, the discrepancy between them representing the difference in the W value caused by the difference in path.

Illustration of the above relation.—For a cycle completed by any system, solid, liquid, or gas, we have seen that $\int dT = 0$, *i.e.* dT is a complete differential. Let us take the particular case of a perfect gas. T being here a function of p and v only, according to the relation—

$$T = \frac{pv}{R}$$

dT is now the complete differential, and we can in this case write T in place of W, v for x and p for y in the above expression, whence we find—

$$\frac{\partial}{\partial x}\left(\frac{\partial W}{\partial y}\right) \text{ becomes } \frac{\partial}{\partial v}\left(\frac{\partial T}{\partial p}\right)$$

and since $T = \frac{pv}{R}$, it follows that $\frac{\partial T}{\partial p} = \frac{v}{R}$

hence $$\frac{\partial}{\partial x}\left(\frac{\partial W}{\partial y}\right) = \frac{\partial}{\partial v}\left(\frac{v}{R}\right) = \frac{1}{R}.$$

Again, we also find that—

$$\frac{\partial}{\partial y}\left(\frac{\partial W}{\partial y}\right) \text{ becomes } \frac{\partial}{\partial p}\left(\frac{\partial T}{\partial v}\right)$$

and since $T = \frac{pv}{R}$, it follows that $\frac{\partial T}{\partial v} = \frac{p}{R}$

and therefore $$\frac{\partial}{\partial y}\left(\frac{\partial W}{\partial x}\right) = \frac{\partial}{\partial p}\left(\frac{p}{R}\right) = \frac{1}{R}.$$

We have therefore reached the same result in both cases, showing thereby the validity of the above mathematical relation in this particular instance.

Further Consideration of the First Law and the Methods of Expressing it in Different Cases.

When some heat is added to a body two changes will in general take place :—

(1) The temperature of the body will increase.

(2) The volume of the body will increase.

Let us regard these two effects, not as occurring simultaneously but as consecutively. That is, we consider that the total effect produced is divided up into (1) an increase of temperature, the volume of the body or system remaining constant, followed by (2) an increase in volume, the temperature remaining constant. In the first stage of the process if the temperature of the body rises dt degrees, the heat which has to be added is $C_v dt$, C_v being the specific heat at constant volume. In the second stage (in *reality*, simultaneously with the temperature change), the volume increases by an amount dv at constant temperature.

Suppose l is the latent heat of expansion of the body, that is the heat which must be added to the body to cause it to increase by unit volume while the temperature is kept constant, then the heat which is required to keep the temperature constant while the volume increases by dv is ldv. Suppose the total amount of heat added to the system is dQ, then it follows from the principle involved in the First Law, that—

$$dQ = C_v dt + ldv.$$

This relation holds good for any system whatsoever, gaseous, liquid, or solid, and holds equally well for homogeneous and heterogeneous systems. With regard to the term l, "the latent heat of expansion," it is so natural to connect latent heat with a fusion or vaporisation process that the student might perhaps think that a heterogeneous system only was being referred to. This is not the case, as, for example, we can imagine a gas expanding at constant temperature, heat having to be added in order to keep the temperature constant. Now let us link this expression up with the equation which we have taken as a statement of the First Law of Thermodynamics, namely—

$$dQ = dU + dA.$$

Since we are considering a system (of any sort whatsoever) which undergoes a volume change against a pressure which may be represented by p, we can then write the term pdv instead of dA. The First Law expression may therefore be put into the shape—

$$dU = dQ - pdv$$

and substituting the value we have found for dQ in the case of a system which undergoes a temperature and volume increase, we obtain for the increase in internal energy the expression—

$$dU = C_v dt + (l - p)dv.$$

Remember this expression holds for any system or substance whatsoever.

Criterion of a Perfect Gas.—The Joule Experiment.

A perfect gas, we have seen from the kinetic standpoint, is one in which molecular attractions are entirely absent. Since this is so, it follows that no *internal* work can be done in separating the molecules from one another when the gas expands. This means that during the expansion no heat goes to do internal work;[1] the heat which in the general case has to be added to keep the temperature constant, namely, the latent heat l, is now required simply to enable the gas to overcome the external resistance pressure p and to do the external work pdv in-

[1] It is evident that the specific heat of a perfect gas is independent of the volume occupied by the gas and likewise independent of the temperature. In a perfect gas we assume that the internal energy is entirely due to kinetic energy of translation of the molecules, *viz.* $\frac{1}{2}$ Nmu², which is identical with $\frac{3}{2}$RT/M if we are considering one gram of gas of molecular weight M. That is, $C_v = \frac{3}{2} \cdot \frac{d}{dT}\left(\frac{RT}{M}\right) = \frac{3}{2}R/M$, an expression which is obviously independent of both volume and temperature.

volved in the volume increase. That is to say, we can regard ldv and pdv as identical numerically, and therefore for a perfect gas we can write the equation—

$$dQ = C_v dt + pdv.$$

This equation does not hold for any other system, however, owing to the presence of cohesion or molecular attraction forces, say in the case of liquids, solids, vapours and indeed ordinary gases, though only to a slight extent in the last named. We have seen that for any system whatsoever, the increase in internal energy dU, when the volume and the temperature of the system increase, is given by the expression—

$$dU = C_v dt + (l - p)dv.$$

Now we have seen from the molecular standpoint that in the case of a perfect gas, no internal work is done in expanding (though there is internal energy represented by U), and hence the latent heat of expansion at constant temperature ldv for the small volume change is identical with the external work pdv, at constant temperature. Hence for a perfect gas the above equation reduces to—

$$dU = C_v dt.$$

This shows that the internal energy U of a given mass of a perfect gas is independent of the volume occupied by the gas (there is no V term in the above equation); and, further, that U depends only on the absolute temperature. When the temperature of a perfect gas is kept constant, *i.e.* when $dt = 0$, then $dU = 0$, or U remains constant, and this even during an expansion against external pressure p, when work pdv is done at the expense of the latent heat which is allowed to stream in. The above criterion of a perfect gas, namely, that its internal energy is independent of the volume, and depends only on the temperature, was first recognised by Joule, who carried out the experiment described in the preceding chapter. The same question is taken up later on (page 52).

Alternative Expression for the First Law in the Case of a Perfect Gas.

It has been pointed out that in the case of a perfect gas only, the First Law can be written in the form $dQ = C_v dt + pdv$. Now we can write this in an alternative form involving C_p instead of C_v, where C_p stands for the specific heat of the gas at constant pressure. Thus, since we are dealing with 1 gram of a perfect gas, then at any stage in the transformation considered we always have the relation $pv = RT$, or $pdv + vdp = Rdt$.

Further $C_p - C_v = R$.[1]

$$\therefore \quad pdv = C_p dt - C_v dt - vdp.$$

[1] This may be easily shown as follows: Consider 1 gram of gas volume v, pressure p, temperature T. We have the relation

$$pv = RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(R being given the correct numerical value for 1 gram, *i.e.* R = 1·9 calories per

Hence $dQ = C_v dt + pdv = C_v dt + C_p dt - C_v dt - vdp$
or $dQ = C_p dt - vdp$.

Remember these relations hold only for a perfect gas. For any other system we are only justified in writing—

$$dQ = C_v dt + ldv.$$

The Second Law of Thermodynamics.

To show that dQ is not a Complete Differential, but that $\frac{dQ}{T}$ *or dS is a Complete Differential.*

If we take any system round a complete cycle, we have already seen that the internal energy U returns to its initial value, and $\int dU = 0$, or in other words dU is a complete differential. We have seen likewise that, having completed a cycle, the expression $\int dA$ is not necessarily zero, and since we must have by the First Law of Thermodynamics the expression $dQ = dU + dA$, it follows that $\int dQ$ may not be zero, that is dQ is not a complete differential. Instead of going round a complete cycle, suppose we take the substance from an initial to a final state, we see as a consequence of the above reasoning that the U of the system depends upon the state in which it is at the moment, and that therefore the difference in U due to the transformation is entirely determined by the initial and final states of the transformation. Such is not the case with the work term. This is not simply dependent on the initial and final states—say the volume occupied by the system at start and finish—but likewise depends on the path followed. If, for instance, the temperature was kept constant, a change in A would have had a certain value, but this would be different if there had been temperature changes *en route*, even if the initial and final volume had been v_1 and v_2 in both cases. Since A is dependent on the path, it follows that heat effects, positive or negative, are also dependent on the path. Neither work nor heat can in fact be looked upon as intrinsic properties of the substance in the same way as internal energy can be regarded. Let us consider a special case, namely, a perfect gas undergoing a reversible transformation in which it does maximum work in expanding, and let us apply the First Law in the form here applicable, namely—

$$dQ = C_v dt + pdv$$

which may be changed for a process involving maximum work to—

$$dQ = C_v dt + \frac{RTdv}{v} = C_v dt + RTd \log v.$$

gram-mole). Suppose the temperature is raised 1° at constant pressure p, the volume increases to v_1 and the heat added is C_p. Again we have the relation

$$pv_1 = R(T + 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Subtracting (2) from (1) we obtain $p(v_1 - v) = R$. That is, the work done in the expansion = R. But the difference between the specific heat at constant pressure and at constant volume respectively is the equivalent of the work done in the expansion for 1°.

$$\therefore C_p - C_v = R.$$

Then considering the whole change from an initial state in which the volume is v_0 and the temperature T_0, to a final state in which the volume is v and the temperature T, we can write—

$$\int_1^2 dQ = \int_{T_0}^{T} C_v dt + \int_{v_0}^{v} RT d \log v.$$

It will be observed that the numerical value of $\int C_v dt$ is simply determined by the limits of the integral T_0 and T. In the case of the expression $\int RT d \log v$ the numerical value is not only dependent on the initial and final values of the volume, namely, V_0 and V, but likewise requires a knowledge of all the temperature changes *en route*, for each little $d \log v$ has to be multiplied by the temperature T *at that moment* before integration is possible. Hence, to evaluate this we must know the path as well as the limiting states. This illustration makes it clear how dA and therefore dQ are incomplete differentials, and at the same time it suggests a change which will give us an expression containing dQ, but at the same time the expression itself will be a complete differential. It is seen that $RT d \log v$ or $RT \frac{dv}{v}$ can be made a perfect differential in certain cases, *e.g.*:—

(1) When an isothermal change is considered, the temperature being constant throughout; and

(2) More generally, even when the change is non-isothermal, *if we divide by* T. The First Law then takes the form for a perfect gas—

$$\frac{dQ}{T} = C_v \frac{dT}{T} + \frac{R dv}{v}.$$

The last term $R\frac{dv}{v}$ no longer contains any indefinite factor, T being now removed. Its integral can be evaluated on simply knowing the initial and final states as regards volume. Similarly the integral of $C_v \frac{dT}{T}$ can still, as in the first instance, be evaluated on simply knowing the initial and final temperature states of the system which has undergone transformation. Hence $\frac{dQ}{T}$ is a complete differential depending upon the initial and final states only. In a complete cycle $\int \frac{dQ}{T} = 0$. For a reversible change the quantity $\frac{dQ}{T}$ is called the change in the entropy of the system, and is denoted by dS. For any reversible change therefore from state (1) to state (2)

$$\int_1^2 \frac{dQ}{T} = \int_{s_0}^{s} dS = C_v \log \frac{T}{T_0} + R \log \frac{V}{V_0}.$$

For a complete cycle when T and V have come back to their original values the terms $\frac{T}{T_0}$, $\frac{V}{V_0}$ become necessarily unity and their logarithms

are zero, so that $\int dS = 0$ for the complete cycle. Remember we have only been considering a reversible cycle, and further, we have restricted ourselves to a perfect gas. We shall see later how this latter restriction may be justifiably removed.

The Entropy Equation of a Perfect Gas.

In the case of a perfect gas undergoing a *reversible* process or change from an initial state (1) in which the temperature is T_0 and the volume V_0, to a second state (2) in which the temperature is T and the volume V, the total heat effect, as we have already seen, is given by the expression—

$$\int_1^2 dQ = \int_{T_0}^{T} C_v dT + \int_{v_0}^{v} RT d \log v.$$

We may slightly transform this expression by dividing across by T. Since the process is reversible we know from the Second Law that $dQ/T = dS$, and we can therefore write—

$$\int_1^2 \frac{dQ}{T} = \int_1^2 dS = \int_{T_0}^{T} C_v \frac{dT}{T} + R\int_{v_0}^{v} d \log v.$$

The term $\int_1^2 dS$ denotes the total change in the entropy of the gas due to the change considered. As written above, the expression is known as a definite integral because the limits (T_0, T, V_0, V) are explicitly stated. We may give the expression a more general significance if we write indefinite integrals in the following manner:—

$$\int dS = \int C_v \frac{dT}{T} + R\int d \log v + \text{constant}.$$

The constant of integration is independent of the particular state in which the system may happen to exist at any time. (The constant necessarily vanishes when we write down a *definite* integral, for in this case we subtract the values characteristic of the initial state from those characteristic of the final state, with the result that the integration constant disappears.) The term $\int dS$ now stands for the entropy possessed by the system under the conditions considered, *i.e.* we have assumed that the lower limit of temperature from which the integration is carried out is absolute zero. Denoting the term $\int dS$ by the symbol S and the integration constant by the symbol S′, we can write—

$$S = \int_0 C_v \frac{dT}{T} + R\int d \log v + S'$$

or

$$S = C_v \log T + R \log v + S'.$$

This expression is known as *the entropy equation of a perfect gas.* If we set $T = 1$ and $v = 1$, then $S = S'$, or S′ is the entropy of the gas at 1° abs. when the volume is 1 c.c. S′ is a constant characteristic of the substance; it cannot be evaluated on the basis of thermodynamics alone.

Other Entropy Relations.

Let us consider any system whatsoever which undergoes a change of some sort. By the First Law we have—

$$dQ = dU + pdv.$$

If the process be carried out *reversibly* we know, on the basis of the Second Law, that $dQ/T = dS$, and therefore

$$TdS = dU + pdv.$$

Hence $$TdS/dT = dU/dT + pdv/dT.$$

If now we consider a reversible process in which the volume is kept constant this expression alters to the following in which partial differentials must be employed to denote that one of the factors is being kept constant:—

$$T\frac{\partial S}{\partial T} = \frac{\partial U}{\partial T}.$$

This is a relation between the change of entropy with temperature and the change of internal energy with temperature in a reversible process in which the volume is maintained constant.

If, instead of keeping the volume constant, we keep the temperature constant and allow the volume to vary, we obtain on differentiation of the expression, $TdS = dU + pdv$, with respect to volume:

$$T\partial S/\partial v = \partial U/\partial v + p$$

or $$\frac{\partial U}{\partial v} = \left(T\frac{\partial S}{\partial v} - p\right).$$

This gives us the relation between the change of internal energy with volume and the change of entropy with volume in the case of any substance whatsoever which is undergoing a reversible change at constant temperature.

The entropy S of any system whatsoever is given by the relation: $S = \int dS = \int dQ/T +$ constant, in which the constant is a constant of integration and cannot be evaluated on the basis of thermodynamics alone. Further, the total entropy S of a system, the system being made up of a number of different parts (*e.g.* a mixture of gases), is simply the sum of the entropies possessed by the parts, *viz.* S_1, S_2, S_3, etc.; for the value of the integral is independent of the path followed (provided only that it be a reversible one) when the system passes from an initial state to a final state. That is, we can conceive of the system as a whole passing from the initial to the final state, or we may conceive of the several parts as being taken from the same initial to the same final state, the total change in entropy being the same in both cases. That is—

$$S = S_1 + S_2 + S_3 + \text{etc.}$$

The Meaning of Entropy in Terms of Molecules.

When we speak of the entropy of a substance we mean some quality or property characteristic of the substance under a particular set of conditions, in the sense that the internal energy, for example, is a

characteristic property. To get an idea of the kind of property we must, of course, think of the system in terms of the molecules composing it. The molecules of a gas are in continuous disordered movement, a gas being in fact a molecular chaos. In the collected Scientific Papers of J. Willard Gibbs (Longmans), the reader will find on page 418 of the first volume a number of unpublished fragments, one subject bearing the title: Entropy as *mixed-up-ness*. This definition of entropy will be understood to a certain extent if we think of a substance as a molecular chaos. Owing to collisions between molecules their motion tends to become more and more disordered until a final stage of disorder is reached. Gibbs considered that the degree of disorder was identical with entropy. When the disorder or chaos is greatest the entropy of a substance is likewise a maximum. This point of view is dealt with at greater length in the first chapter of Vol. III.

Recently, another term has been employed to describe entropy. This term is "run-down-ness," the entropy denoting the degree of run-down-ness of a system (*cf.* Tolman, *Phys. Rev.*, March, 1917). A system in equilibrium is supposed to have run down as far as possible (compatible with the external conditions and the total energy). At equilibrium, therefore, the entropy of the system is a maximum.

Further Remarks on the Carnot Cycle.

For any completed reversible cycle, and therefore for the particular case of a *Carnot Cycle* (which has been studied in the elementary treatment, Chap. I.), we know from previous consideration that $\int dU = 0$, *i.e.* the U is once more at its original value. Similarly $\int dS = 0$, *i.e.* the entropy of the system is once more at its original value when the cycle is complete. Since internal energy and entropy depend only on the initial and final states, and these states are, of course, identical for a complete cycle, the entropy and internal energy do not depend on the path followed. The expression $\int dA$ is, however, not zero, *i.e.* there has been a nett gain or loss of external work by the system, and hence $\int dQ$ is not zero; there has been a nett addition or subtraction of heat energy to or from the system to balance the work done by or done on the system at some stage or stages of the transformation. Let us see what these work and heat terms are in the special case of a Carnot Cycle.

As we passed isothermally along AB (see Fig. 9), the system took in an amount of heat Q_1 from the infinite heat reservoir. The change in entropy in going from A to B is therefore

$$\int_0^{Q_1} \frac{dQ}{T}$$

which, since T_1 is kept constant, may be written—

$$\frac{1}{T_1}\int_0^{Q_1} dQ, \quad \text{or simply} \quad \frac{Q_1}{T_1}.$$

In passing along BC no heat is taken in or given out, and therefore $dQ = 0$, and hence the entropy change along BC is zero, *i.e.* the entropy at C is the same as at B. (Remember we do not know how *much* this is, we can only deal with changes in entropy, such as $\frac{Q_1}{T_1}$ for the AB transformation.) In passing from C to D isothermally, the entropy change is $-\frac{Q_2}{T_2}$, the temperature being maintained constant, and the minus sign being used to denote that the transfer of heat (in this case an evolution of heat by the system), is in the opposite direction to the heat transfer at T_1, which involved an absorption of heat. Passing from D to A the heat transfer in either direction is nil. On the whole cycle the total change in entropy is—

$$\frac{Q_1}{T_1} + \left(-\frac{Q_2}{T_2}\right)$$

and this must be zero, since $\int dS = 0$.

Hence
$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Although the entropy change is zero on the whole cycle, the heat change is not zero, it being evidently $(Q_1 - Q_2)$, this being the amount of heat equivalent to the work done by the system, for $\int dU = 0$, and always $\int dQ = \int dU + \int dA$. Call this nett total work A. Then

$$A = Q_1 - Q_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we suppose $Q_1 > Q_2$, $Q_1 - Q_2$ is positive, and nett work is done *by* the system. Substituting in (2) the value of Q_2 given by equation (1), we obtain

$$A = Q_1\left(1 - \frac{T_2}{T_1}\right) \quad . \quad . \quad . \quad . \quad (3)$$

In words this expression states that only a fraction of the heat Q_1 which is admitted to the gas at the high temperature T_1 is converted into useful work. If we express the work as a fraction of the heat taken in at the higher temperature, we have—

$$\frac{A}{Q_1} = \frac{T_1 - T_2}{T_1} \quad . \quad . \quad . \quad . \quad (4)$$

This "fractional" work is simply the efficiency η of the engine, and the efficiency of this reversible engine (*i.e.* the gas) depends therefore only on the temperature limits T_1 and T_2. It does not depend on the absolute size of the engine, *i.e.* on the absolute amounts of heat taken in or given out. The efficiency of every reversible engine is therefore the same as long as it works between the same temperature limits, *i.e.* temperature of the "boiler," and the temperature of the "condenser". Besides showing that the efficiency of every reversible engine was the same, if the temperature limits were the same, Carnot showed that no engine can be more efficient than a reversible one (Carnot's Theorem).[1]

[1] For consideration of this see Partington's *Thermodynamics*.

Granting the validity of these two generalisations, we see that we need no longer restrict a Carnot Cycle—or the conclusions which we have come to regarding the relation of A to Q_1—simply to a perfect gas. Any system, solid, liquid, or gas, may be conceived of as being taken round the cycle. Hence for *any* system working as a reversible cycle we have the relation—

$$A = Q_1\left(1 - \frac{T_2}{T_1}\right)$$

or if the temperature differences be denoted by dT, and the work by dA, we have—

$$dA = Q\frac{dT}{T}.$$

Remember that A or dA, *i.e.* the area ABCD, only represents the external or "useful" work. In the case of a perfect gas, we have no other kind of work to deal with. For an imperfect gas, or a liquid, etc., expansions and compressions involve internal work as well. These, however, do not enter into the discussion, and do not vitiate the generality of the results of equations (3) and (4) (p. 49). As long as the process is reversible $\int dS$ or $\int\frac{dQ}{T}$ is zero for any completed cycle, that is, dS is a complete differential. Not only is T an "integrating factor" for the equation of a perfect gas, it is likewise one for all substances, as follows from the two generalisations of Carnot.

The expression connecting the maximum work done by an engine with the heat taken in from the boiler (Q_1 at T_1) may be regarded as a quantitative statement of the Second Law of Thermodynamics, which we have already seen is stated in general terms by Clausius thus: "It is impossible for a self-acting machine working in a cycle, unaided by any external agency, to convey heat from a body at a low temperature to one at a higher temperature, or heat cannot of itself (*i.e.* without the performance of work by some external agency) pass from a cold to a warmer body."

Combination of the First and Second Laws.

I. *An Expression for the Latent Heat of Expansion.*

For any system, solid, liquid, or gas, which is undergoing a volume and temperature change, whether reversibly or irreversibly, we have seen (p. 42) by the First Law of Thermodynamics that

$$dQ = C_v dt + l dv$$

and by a purely algebraical change we can write this—

$$\frac{dQ}{T} = \frac{C_v dt}{T} + \frac{l dv}{T}.$$

If now we consider any system, solid, liquid, or gas, going through a transformation with the restriction that this transformation is a re-

versible one, the Second Law of Thermodynamics tells us that the quantity $\frac{dQ}{T}$ is a complete differential, and we have denoted this by the term dS, which stands for change of entropy of the system. So that both laws applied simultaneously lead to the expression for *any* system changing in a reversible manner—

$$d\mathrm{S} = \frac{\mathrm{C}_v dt}{\mathrm{T}} + \frac{l}{\mathrm{T}} dv.$$

Since dS is a complete differential we can perform the mathematical operation already discussed in connection with complete differentials, arriving at the expression—

$$\frac{\partial}{\partial v}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right) = \frac{\partial}{\partial \mathrm{T}}\left(\frac{\partial \mathrm{S}}{\partial v}\right)$$

or

$$\frac{1}{\mathrm{T}}\frac{\partial \mathrm{C}_v}{\partial v} = \frac{1}{\mathrm{T}}\frac{\partial l}{\partial \mathrm{T}} - \frac{l}{\mathrm{T}^2}$$

or

$$\frac{\partial \mathrm{C}_v}{\partial v} = \frac{\partial l}{\partial \mathrm{T}} - \frac{l}{\mathrm{T}} \quad . \quad . \quad . \quad . \quad (1)$$

We have also seen (p. 42) that for any system—

$$d\mathrm{U} = \mathrm{C}_v dt + (l - p)dv$$

(this being derived without introducing the Second Law).

Since dU is a complete differential, it follows by partial differentiation that—

$$\frac{\partial \mathrm{C}_v}{\partial v}^{1} = \frac{\partial l}{\partial \mathrm{T}} - \frac{\partial p}{\partial \mathrm{T}} \quad . \quad . \quad . \quad . \quad (2)$$

By combining expressions (1) and (2) we obtain—

$$l = \mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_v \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This is an important relation already obtained in the preceding chapter. l, it will be remembered, is the latent heat of expansion, namely, the heat required to keep the temperature of the system (solid, liquid, or gas) constant while unit increase in volume takes place. Note that this is not necessarily latent heat of vaporisation (*i.e.* volume

[1] The expression $\left(\frac{\partial \mathrm{C}_v}{\partial v}\right)_\mathrm{T}$ represents the change in the specific heat at constant volume with the volume, the temperature being maintained constant. The meaning of this sometimes is a source of difficulty. Suppose you take a system at (large) volume v_1, and measure the specific heat, keeping the volume constant at v_1, you get a certain value for C_v. Suppose you take the same system at a different volume v_2 (brought about by a change in pressure) and again measure the specific heat, keeping the volume constant at v_2, you again get a value for C_v, which may not be the same as in the first case. The difference of the two values of C_v divided by the difference of $v_1 - v_2$ would be $\frac{d\mathrm{C}_v}{dv}$. If you have carried out the two determinations at the same mean temperature, the difference of the two values of C_v divided by $v_1 - v_2$ gives you $\left(\frac{\partial \mathrm{C}_v}{\partial v}\right)_\mathrm{T}$.

change in a heterogeneous system containing liquid and vapour), but equally applies to a volume change taking place in a purely homogeneous system.

II. *The Joule Experiment and the Criterion of a Perfect Gas from the standpoint of the two Laws of Thermodynamics.*

We have already seen that the increase in the internal energy of any system may be expressed—

$$dU = C_v dt + (l - p)dv.$$

Substituting for l its value $T\left(\frac{\partial p}{\partial T}\right)_v$ we obtain—

$$dU = C_v dt + \left(T\frac{\partial p}{\partial T} - p\right)dv.$$

Now it has been shown that the internal energy of a perfect gas would be independent of the volume occupied, and would depend only on the temperature (Joule's Law). Hence, applying the above expression to the case of a perfect gas, in order to make dU independent of v, it is necessary to consider—

$$T\frac{\partial p}{\partial T} - p = 0.$$

This differential equation is satisfied by the relation—

$$p = Tf(v)$$

where $f(v)$ is simply an integration constant independent of T. It should be noted that whilst this expression is a criterion of a perfect gas, other substances might conceivably satisfy it. We shall come to this point later in discussing the Joule-Thomson experiment.

III. *The Clapeyron Equation.*

The deduction of this expression need not be further given, as it has already been considered in the Elementary Treatment. It is of interest, however, to discuss briefly the quantities denoted by the terms internal and external latent heat.

External and Internal Latent Heat of Vaporisation.

In the process of vaporisation, the heat which we add, namely, λ calories per gram, to keep the temperature constant may be divided into two parts.

1. Part of the heat goes to overcome the internal cohesive forces (which are very large in the liquid state).

2. Part of the heat goes to do the external work of expansion against the pressure exerted by the vapour.

The first part is called the internal latent heat, and may be represented by λ_i. The second part is the external latent heat or heat used

purely in doing external work (namely, vapour pressure × volume increase), and may be represented by λ_{ex}. That is

$$\lambda = \lambda_i + \lambda_{ex}.$$

We can obtain an approximate value for the external latent heat as follows:—

Take the case of water. Neglect the specific volume of liquid compared to the specific volume of steam. Work of expansion $= p(v_1 - v_0) = pv_1$. Apply the gas law to the steam as an approximation. Then $pv_1 = RT$, where R refers to 1 gram, *i.e.* $R = \frac{2}{18} = \frac{1}{9}$ calories approx. Suppose we consider the boiling point of water. $T = 373$. Then $pv_1 = \frac{373}{9} = 41$ calories approx. $= \lambda_{ex}$. The total latent heat λ is approx. 536 calories at 100° C., so that practically 500 calories (*i.e.* λ_i) are required for the internal work against the cohesive forces. The following table contains some of the values given by Zeuner (*cf.* Chwolson, *Lehrbuch der Physik*, vol. iii. p. 654) for the case of *water*:—

$t°$ C.	Vapour Pressure in mms. Hg.	$\frac{dp}{dt}$.	λ Observed.	λ_i.	λ_{ex}.
			Cals.	Cals.	Cals.
− 10	2·093	0·1611	613·45	583·15	30·30
0	4·600	0·329	606·50	575·43	31·07
50	91·98	4·580	571·66	536·12	35·54
100	760·00	27·19	536·50	496·30	40·20
150	3,581·2	96·17	500·79	456·70	44·09
200	17,689·0	243·44	464·30	417·70	47·13

If we wish to use λ_i instead of λ in the Clapeyron equation, it may be transformed into—

$$\lambda_i = T(v_1 - v_0)\frac{dp}{dt} - p(v_1 - v_0) = \left(T\frac{dp}{dt} - p\right)(v_1 - v_0)$$

which yields, when v_0 as compared to v_1 is neglected and the vapour is treated as a perfect gas—

$$\lambda_i = RT^2\frac{d \log p}{dt} - RT = RT\left(T\frac{d \log p}{dt} - 1\right).$$

IV. *Thermodynamic Expressions dealing with Specific Heat.*

Let us return to the expression for the latent heat of expansion l—for any system, homogeneous or heterogeneous—namely—

$$l = T\left(\frac{\partial p}{\partial T}\right)_v \text{ (equation (3), p. 51).}$$

Differentiating this expression with respect to T, keeping the volume constant, we obtain—

$$\left(\frac{\partial l}{\partial T}\right)_v = \left(\frac{\partial p}{\partial T}\right)_v + T\left(\frac{\partial^2 p}{\partial T^2}\right)_v.$$

Now, we have already seen (p. 51) that for any system—

$$\left(\frac{\partial C_v}{\partial v}\right)_T = \left(\frac{\partial l}{\partial T}\right)_v - \left(\frac{\partial p}{\partial T}\right)_v.$$

Combining these two expressions, we obtain—

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v.$$

This important relation will be taken up later in connection with the continuity of state.

A second important relation, dealing with the difference of the specific heats at constant pressure and volume respectively, must be considered. To get at this, we must go back to some of our earlier considerations. If we take any system whatsoever from a certain p, V, T, to another state in which p, V, T, have different values, we saw that we had to add a quantity of heat which, for very small transformations, we denoted by dQ. The absorption of this heat by the system was artificially divided up into two consecutive processes, *viz.* :—

First.—The temperature rose by an amount dt, the volume being kept constant. The heat absorbed amounted to $C_v dt$ (of course, the pressure increased in this process, as we see when we use the term C_v).

Second.—The system was caused to expand, the temperature being kept constant; the requisite heat for this stage being $l dv$, where l is the latent heat of expansion. (In this process also, the pressure underwent changes concomitant with the volume change.) These two processes added together give us the heat absorption for the total transformation, the expression obtained being—

$$dQ = C_v dt + l dv$$

which on substituting equation (3), p. 51, for l becomes—

$$dQ = C_v dt + T\left(\frac{\partial p}{\partial T}\right)_v dv.$$

Now let us think of the total transformation, when we are dealing with the same heat absorption dQ, but let us artificially break up the process into two stages which differ from the preceding, namely—

First.—Let the temperature of the system be raised by an amount dt, the pressure being kept constant. The heat absorption is $C_p dt$, where C_p is the specific heat of the system at constant pressure. (In this process naturally, the volume must have undergone a concomitant change.)

Second.—Having now the system at the final temperature value, suppose this to be kept constant, and let us consider that the pressure of the system is now allowed to rise by the amount dp. This involves an absorption of heat $l' dp$, when l' is the latent heat of pressure change. (Naturally in this last process the volume must have changed concomitantly with the pressure.) These two processes added together have been assumed to give the same total heat dQ. For this case therefore we have—

$$dQ = C_p dt + l' dp.$$

Dividing across by T, and assuming that the process has been carried out in a reversible manner, we obtain—

$$\frac{dQ}{T} \text{ or } dS = \frac{C_p dt}{T} + \frac{l' dp}{T}$$

and since dS is a complete differential we can as usual write—

$$\frac{\partial}{\partial p}\left(\frac{C_p}{T}\right) = \frac{\partial}{\partial T}\left(\frac{l'}{T}\right)$$

or

$$\frac{1}{T}\left(\frac{\partial C_p}{\partial p}\right)_T = \frac{1}{T}\frac{\partial l'}{\partial T} - \frac{l'}{T^2}$$

or

$$\frac{\partial C_p}{\partial p} = \frac{\partial l'}{\partial T} - \frac{l'}{T} \quad . \quad . \quad . \quad . \quad (1)$$

Again, by the First Law of Thermodynamics for any substance—

$$dQ = dU + dA$$

or

$$dQ = dU + p dv$$

$$\therefore dU = dQ - p dv$$

$$\therefore dU = C_p dt + l' dp - p dv$$

and by a simple mathematical transformation—

$$d(U + pv) = C_p dt + l' dp + v dp$$
$$= C_p dt + (l' + v) dp.$$

Now since dU is a complete differential, and since on completing a cycle the p and v return to their original values, it follows that $d(pv)$ is a complete differential, and therefore $d(U + pv)$ is likewise one, and hence from the above equation we obtain by partial differentiation—

$$\frac{\partial C_p}{\partial p} = \frac{\partial l'}{\partial T} + \frac{\partial v}{\partial T} \quad . \quad . \quad . \quad . \quad (2)$$

By combining (1) and (2) one finds—

$$l' = -T\left(\frac{\partial v}{\partial T}\right)_p.$$

Hence the equation—

$$dQ = C_p dt + l' dp$$

may be put in the form—

$$dQ = C_p dt - T\left(\frac{\partial v}{\partial T}\right)_p dp \, . \quad . \quad . \quad . \quad (3)$$

Now in the alternative method of splitting up dQ into parts containing dt and dv respectively, we have already seen that—

$$dQ = C_v dt + T\left(\frac{\partial p}{\partial T}\right)_v dv \, . \quad . \quad . \quad . \quad (4)$$

Equations (3) and (4) must be identical, for we considered the same system starting from the same point and ending at another given point the same for both, and further we have assumed that the changes are reversible in both cases. Hence, equating (3) and (4), we get—

$$(C_p - C_v) dT = T\left(\frac{\partial v}{\partial T}\right)_p dp + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

or

$$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p \cdot \frac{dp}{dT} + T\left(\frac{\partial p}{\partial T}\right)_v \cdot \frac{dv}{dT}$$

Now as a purely mathematical operation, if p is a function of T and V, *i.e.* if $p = f(T, V)$, we have a connection between the ordinary differential $\frac{dp}{dT}$ (which means variation of p with T, while v at the same time varies), and the partial differential $\frac{\partial p}{\partial T}$ (which means variation of p with T when v is kept constant).

This connection is expressed thus—

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial T}\right)_v + \left(\frac{\partial p}{\partial v}\right)_T \cdot \frac{dv}{dT}.$$

Substituting this value of $\frac{dp}{dT}$ in the preceding equation, we get—

$$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p \left\{\left(\frac{\partial p}{\partial T}\right)_v + \left(\frac{\partial p}{\partial v}\right)_T \cdot \frac{dv}{dT}\right\} + T\left(\frac{\partial p}{\partial T}\right)_v \cdot \frac{dv}{dT}$$

or $$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p \cdot \left(\frac{\partial p}{\partial T}\right)_v \cdot + T\left[\left(\frac{\partial v}{\partial T}\right)_p \cdot \left(\frac{\partial p}{\partial v}\right)_T + \left(\frac{\partial p}{\partial T}\right)_v\right]\frac{dv}{dT}.$$

Now a further general mathematical relation has to be here made use of, namely, if we have three variables x, y, and z which are mutually dependent, then in all cases we can write—

$$\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1.$$

Using the three variables p, v, T, we can write—

$$\left(\frac{\partial p}{\partial T}\right)_v \cdot \left(\frac{\partial T}{\partial v}\right)_p \cdot \left(\frac{\partial v}{\partial p}\right)_T = -1.$$

Substituting this in the preceding equation, we see that—

$$\left[\left(\frac{\partial v}{\partial T}\right)_p \cdot \left(\frac{\partial p}{\partial v}\right)_T + \left(\frac{\partial p}{\partial T}\right)_v\right] = 0$$

and therefore $$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p \cdot \left(\frac{\partial p}{\partial T}\right)_v \quad . \quad . \quad . \quad (5)$$

And this holds for any substance whatsoever. It will be referred to later in the next chapter, dealing with Continuity of State.

Addendum.

The expression for $(C_p - C_v)$, *viz.* equation (5), as well as that for l', *viz.* $l' = -T\left(\frac{\partial v}{\partial T}\right)_p$ may be obtained by a shorter method than that adopted above. This method, for which the writer is indebted to Lieut. W. T. Duncan, is as follows:—

In any infinitesimal transformation whatever, the heat absorbed is given, as we have seen, by the expression—

$$dQ = C_v dT + l dv,$$

As this expression is perfectly general, we may restrict $d'T$ and dv to be such that the pressure remains constant during the transformation, and when this is so we can substitute $C_p d'T$ for $d'Q$, writing at the same time $dv = \left(\frac{\partial v}{\partial T}\right)_p d'T$.

Hence the above equation becomes—

$$C_p d'T = C_v d'T + l\left(\frac{\partial v}{\partial T}\right)_p . d'T$$

or

$$C_p - C_v = l\left(\frac{\partial v}{\partial T}\right)_p$$

But it has already been shown that $l = T\left(\frac{\partial p}{\partial T}\right)_v$

and therefore

$$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v .$$

To obtain the expression for l' we may write down the general equation

$$d'Q = C_p d'T + l' dp.$$

Let this represent a transformation at constant volume. It can then be written—

$$C_v d'T = C_p d'T + l'\left(\frac{\partial p}{\partial T}\right)_v d'T$$

or

$$C_p - C_v = - l'\left(\frac{\partial p}{\partial T}\right)_v .$$

But

$$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v$$

therefore

$$- l'\left(\frac{\partial p}{\partial T}\right)_v = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v$$

or

$$l' = - T\left(\frac{\partial v}{\partial T}\right)_p .$$

CHAPTER III.

Continuity of the liquid and gaseous states from the thermodynamic standpoint.

Continuity of State from the Thermodynamic Standpoint.

In the preceding chapter we have deduced several important relations on the basis of thermodynamics, and we have now to see what conclusions they lead to when applied to the equilibrium conditions which obtain in the distribution of matter in space, under varying conditions of temperature and pressure. It is proposed therefore to review again the more important equations of state already treated from the molecular kinetic standpoint (Vol. I. chap. ii.). It will be seen that the introduction of these general thermodynamic theorems considerably enlarges the number of conclusions which we are able to draw from the respective equations of state, with regard to the behaviour of gas or liquid systems. By comparing the theoretical conclusions with actual experimental results we gain a further insight into the limits of applicability of our equations of state and the assumptions upon which they rest. In this way we are able to discriminate to a large extent between conflicting theories and assumptions.

The relations which we may first consider are—

$$l = \mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_v$$

and

$$\mathrm{T}\left(\frac{\partial^2 p}{\partial \mathrm{T}^2}\right)_v = \left(\frac{\partial \mathrm{C}_v}{\partial v}\right)_\mathrm{T}.$$

In the first of the above relations l stands for the latent heat of expansion, that is, the heat which has to be added to a system to keep the temperature constant while the volume increases by unity. As already pointed out, this relation may be applied to homogeneous and heterogeneous systems alike. For the present we shall consider homogeneous systems only, *i.e.* systems consisting entirely of gas or entirely of liquid.

First take the case of a perfect gas. The characteristic equation for such a body is—

$$pv = \mathrm{RT}.$$

We have already seen (p. 43) that for the expansion ∂v of a perfect gas against a pressure p the following holds good, *viz.* :—

$$ldv = pdv.$$

No heat is taken in to do internal work, and therefore there must be no internal work to do. This is a thermodynamic proof of the conclusion to which we have already come on kinetic considerations, viz. that there are no cohesive forces existing between the molecules of a perfect gas, and therefore there can be no internal work done on expanding (*cf.* Joule's experiment (p. 20)). Further, since for a perfect gas—

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$$

it follows that on again differentiating with respect to T, keeping v constant,

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0,$$

for both R and v are constant. Therefore, from the second thermodynamic relation (p. 58) considered it follows that—

$$\left(\frac{\partial C_v}{\partial v}\right)_T = 0.$$

In other words, the specific heat of a perfect gas at constant volume is independent of the absolute magnitude of the volume. That is, suppose we consider one gram of a perfect gas occupying a volume v, and we raise the temperature 1°, keeping the volume at v, we require to add a certain quantity of heat C_v. If we consider the same *mass of gas* at the same temperature as before, and at quite a different volume v_1 (the pressure being, of course, different now), and we raise the temperature 1°, keeping v_1 constant, it will be found that the amount of heat required is again C_v.

Comparison of Some of the Equations of State.

There is no such thing in nature, however, as a perfect gas. Let us therefore consider actual gases, and let us suppose that we can apply VAN DER WAALS' EQUATION—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

From this we obtain by differentiation—

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - b},$$

therefore

$$l = \frac{RT}{v - b} = p + \frac{a}{v^2}$$

or

$$l\,dv = p\,dv + \frac{a}{v^2}dv.$$

In words, for an expansion dv the heat which has to be added to keep the temperature constant, *viz.* ($l\,dv$), is equal to the external work done ($p\,dv$) plus the internal work done $\left(\frac{a}{v^2}dv\right)$ against the cohesive force

$\left(\frac{a}{v^2}\right)$. Thus, for a van der Waals gas the heat entry at constant temperature is greater than the heat which has to be added in the case of a perfect gas, by the amount representing the internal work done.

Again, on differentiating the equation—

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - b}$$

with respect to T at constant v, we obtain—

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = \frac{\partial}{\partial T}\left(\frac{R}{v - b}\right)_v = 0,$$

therefore

$$\frac{\partial C_v}{\partial v} = 0,$$

i.e. van der Waals' equation leads to the conclusion that the specific heat at constant volume of an imperfect gas (one obeying van der Waals' equation) is independent of the volume. (The same conclusion was reached in the case of a perfect gas.) This conclusion is, however, not borne out in practice, as the value of C_v is found not to be independent of volume (v). In general as v increases C_v diminishes, though sometimes the reverse is the case. The following examples are quoted by Kuenen (*Die Zustandsgleichung*, p. 118, from Reinganum, *Dissertation*, Göttingen, 1899). In order to deal with different values of v, the smaller limit for this quantity refers to the substance entirely in the liquid state, the higher limit referring to the substance (at the same temperature) completely in the state of vapour.

Substance.	C_v Liquid. v Very Small.	C_v Vapour. v Large.
Ether	0·358	0·346
Carbon disulphide . .	0·160	0·131 (Regnault) 0·105 (Wiedemann)
Chloroform	0·156	0·140 (Regnault) 0·115 (Wiedemann)

In the case of carbon-dioxide, Dieterici (*Annalen der Physik*, [4], **12**, 173, 1903) states that the C_v for small values (1·1—1·125 c.c.) is 0·24 and that it *increases* with increasing volume, reaching a maximum $C_v = 0{\cdot}34$ in the neighbourhood of the critical volume, and then decreases with further increase in volume. An analogous behaviour was observed in the case of isopentane. *Cf.* M. Reinganum (*Annalen der Physik*, **18**, 1008, 1905).

The Ramsay and Young Equation of State may be put in the form—

$$p = Tf(v) - F(v)$$

and, as already pointed out, the van der Waals equation is a special

case of this, so that this relation leads to the same conclusions regarding C_v as those already obtained. Thus—

$$\left(\frac{\partial p}{\partial T}\right)_v = f(v)$$

$$l = T\left(\frac{\partial p}{\partial T}\right)_v = Tf(v) = p + F(v)$$

or $$ldv = pdv + F(v)dv.$$

If we substitute $\frac{a}{v^2}$ for $F(v)$ we get the van der Waals result.

Similarly—

$$\left(\frac{\partial^2 p}{\partial T^2}\right) = \frac{\partial}{\partial T_v}(f(v)) = 0 \text{ as before.}$$

Now let us see to what conclusions the CLAUSIUS EQUATION leads when treated in the same manner. This equation, it will be remembered, differs from van der Waals' or Ramsay and Young's in that the cohesive force was considered to vary with the temperature, and at the same time was a more complex function of the density. The equation is—

$$p = \frac{RT}{v - b} - \frac{a}{T(v + c)v}.$$

In this case—

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - b} + \frac{a}{T^2(v + c)v}.$$

$$\therefore T\left(\frac{\partial p}{\partial T}\right)_v = \frac{RT}{v - b} + \frac{a}{T(v + c)v}$$

$$= p + \frac{a}{T(v + c)v} + \frac{a}{T(v + c)v}$$

$$= p + \frac{2a}{T(v + c)v}.$$

$$\therefore l = T\left(\frac{\partial p}{\partial T}\right)_v = p + \frac{2a}{T(v + c)v}$$

or $$ldv = pdv + \frac{2a}{T(v + c)v} \cdot dv.$$

In words, this means that the heat which has to be added to keep the temperature of the gas (or liquid) constant while a volume increase takes place is equal to the external work done in expansion plus *twice* the internal work done in expansion. In this case therefore when the volume changes the heat entry is *not* equal to the external + the internal work as in the case of a van der Waals substance, but there is an extra indraught as well. In this case the extra indraught happens to be just equal to the internal work done, *viz.*—

$$\frac{a}{T(v + c)v} \cdot dv.$$

Further, it is seen that—

$$T\left(\frac{\partial^2 p}{\partial T^2}\right)_v = -\frac{2aT}{T^3(v+c)v}$$

and therefore $\left(\frac{\partial C_v}{\partial v}\right)_T$ = a negative quantity,

i.e. the specific heat measured when the volume is kept constant during the 1° rise should decrease when the mass employed is caused to occupy a greater volume, *i.e.* by working at different pressures. There is no evidence of a change of sign such as that actually exhibited by carbon-dioxide and isopentane.

Again, let us take the DIETERICI EQUATION—

$$p = \frac{RT}{v-b} \cdot e^{\frac{-a}{T^n v}}$$

which may be written in the form—

$$\log p = \log T + \log \frac{R}{v-b} - \frac{a}{T^n v}$$

whence $\left(\frac{\partial p}{\partial T}\right)_v = \frac{p}{T} + \frac{anp}{vT^{n+1}}$,

or $l = T\left(\frac{\partial p}{\partial T}\right)_v = p + \frac{npa}{vT^n}$

hence $ldv = pdv + \frac{npa}{vT^n} \cdot dv$,

i.e. heat which is required to be added to keep the temperature constant = the external work done plus a positive quantity due to internal work, to which no simple physical meaning can be attached.

APPLICATION OF THE THERMODYNAMIC RELATION :—

$$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v \quad \text{(see p. 56).}$$

For a perfect gas—

$$pv = RT$$

whence $\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$ and $\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$

therefore $T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v = \frac{R^2T}{pv} = R$

therefore $C_p - C_v = R$, a result to which we have already come (p. 44, footnote).

For a substance obeying van der Waals' expression we would have—

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

therefore $\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$, therefore $T\left(\frac{\partial p}{\partial T}\right)_v = \frac{RT}{v-b}$.

Also to get $\left(\frac{\partial v}{\partial T}\right)_p$ we may differentiate van der Waals' equation as given above. Remembering that p is constant, and therefore $\left(\frac{\partial p}{\partial T}\right)_p = 0$, we find—

$$0 = \frac{R}{v - b} - \frac{RT}{(v - b)^2}\left(\frac{\partial v}{\partial T}\right)_p + \frac{2a}{v^3}\left(\frac{\partial v}{\partial T}\right)_p.$$

$$\therefore \left(\frac{dv}{\partial T}\right)_p = \frac{\frac{R}{v - b}}{\frac{RT}{(v - b)^2} - \frac{2a}{v^3}}$$

$$\therefore C_p - C_v = \frac{\frac{RT}{v - b} \cdot \frac{R}{v - b}}{\frac{RT}{(v - b)^2} - \frac{2a}{v^3}}$$

$$= \frac{R}{1 - \frac{2a(v - b)^2}{RTv^3}}.$$

Since the denominator is less than unity, the expression for $C_p - C_v$ is greater than R, the extra amount being due to the cohesion effects between the molecules. The following short table gives some experimental values obtained for C_p and C_v (in the region of room temperature). No attempt is made to compare these values with the above expression, owing to the doubt which exists as to what values should be taken for a and b (since they are not quite constant) and $(C_p - C_v)$ being a small quantity, the calculation would be sensitive to numerical errors. The values show, as might have been expected, that at this temperature oxygen (O_2) and hydrogen (H_2) approximate very nearly to perfect gases, whilst $(C_p - C_v)$ is in the cases of ammonia and carbon dioxide distinctly greater than R.

Gas.	C_v per gram.	C_p per gram.	$(C_p - C_v)$ per mole.	R per mole in calories.
Perfect gas . . .	—	—	1·985	1·985
Hydrogen . . .	2·4211	3·4090	1·976	
Oxygen	0·1556	0·2175	1·981	
Ammonia . . .	0·3951	0·5205	2·108	
Carbon dioxide . .	0·1669	0·2169	2·20	

The value $(C_p - C_v)$ calculated on the Dieterici equation is very complicated and need not be given here.

The Porous Plug Experiment of Joule and Thomson and the Phenomena of Inversion Points.

This experimental investigation was carried out as an extension of the Joule experiment already alluded to, with the object of finding by much more refined methods the divergencies of real gases from the requirements of the perfect gas. The conditions of the present experiment, however, differ in principle from that of the Joule experiment, and it must be clearly borne in mind that the conclusions to be drawn from each are different. In the porous plug experiment, as the name suggests, a gas was forced through a resistance consisting of a diaphragm fitted with a fine opening, situated in the axis of a wider tube. A diagrammatic sketch is given in Fig. 12. Owing to the resistance of the plug, the pressure was higher on one side than on the other, and it was shown by means of a sensitive thermometer placed at the plug that on the low-pressure side the temperature was less than that on the high-pressure side. This behaviour was exhibited by all the gases examined by them with the exception of hydrogen, which was found to be at a higher temperature on the low-pressure side. On passing through the

Fig. 12.

plug, therefore, most gases are cooled, hydrogen being warmed; the experiment being carried out in the region of atmospheric temperature. When, however, the experiment is carried out at a sufficiently low temperature, there is a cooling even in the case of hydrogen on passing through the plug. This behaviour suggests the existence of an inversion point (or more than one, as we shall see later) for all substances, at which point there would be neither cooling nor heating on passing through the plug. Joule and Thomson found that the cooling, *i.e.* the fall in temperature produced, was proportional to the difference in pressure on the two sides of the plug. That is if $-\Delta t$ represents the cooling, then $-\Delta t = k(p_1 - p_0)$, where $(p_1 - p_0)$ is the difference of pressure and k is a constant characteristic of the fluid under examination and is the fall of temperature for 1 atmosphere difference in pressure. At atmospheric temperature in the case of air, it was found that $k = 0{\cdot}262°$; for carbon dioxide $k = 1{\cdot}225°$. For hydrogen k is negative. Natanson found later in the case of CO_2 at 20° C. that k increases somewhat with the pressure. Joule and Thomson further found that k is inversely proportional to T^2, that is—

$$k = \frac{A}{T^2}.$$

Rose-Innes (*Phil. Mag.*, **45**, 227, 1898) found that the results

obtained by Joule and Thomson for the cooling (k) per 1 atmosphere pressure difference could also be represented by the formula—

$$k = A - \frac{B}{T}.$$

It may be pointed out that the Rose-Innes formula, if a valid one, indicates that a point of inversion must exist, *i.e.* when $A = \frac{B}{T}$ or $T = \frac{B}{A}$ so that it agrees with the observation already referred to and obtained by Olszweski in 1901 in the case of hydrogen. Now the cause of the thermal effect is the divergence of the gases from the perfect state. These effects may be divided into deviations from—

(1) Boyle's Law. (Boyle's Law states $(pv)_T$ = constant.)

(2) Joule's Law. (Joule's Law states that U = KT and is independent of volume.)

The deviations from Boyle's Law may be separately examined, as has already been done in dealing with the $pv \times p$ diagram of Amagat (Vol. I. chap. ii.). If we could eliminate this we could get the deviation from Joule's Law. Consider in the diagram of the tube (Fig. 12) two points, A and B, sufficiently far removed from the plug itself that the gas flow is steady at these points. Suppose A is on the high-pressure side and suppose further that U_1 is the internal energy of 1 gram of gas at the point A, and U_2 is the internal energy of 1 gram of gas at the point B. Consider the block of gas AB. Suppose it to move so as to occupy the volume A_1B_1. There is the same mass of gas in the slab AA_1 as there is in BB_1, though of course the volumes are different, since the pressures are different. Suppose for simplicity that each slab contains 1 gram of gas. Further, let $AA_1 = V_1$ and $BB_1 = V_2$. In forcing the block of gas AB through the tube containing the plug the work done *on* the gas at the high-pressure side is p_1v_1, when p_1 is the high pressure. The work done *by* the gas on the low-pressure side is p_2v_2. The net work done on the gas equals $p_1v_1 - p_2v_2$.

This is a gain in energy, since heat has been neither added nor subtracted. The net gain in energy is $U_2 - U_1$;

therefore $$p_1v_1 - p_2v_2 = U_2 - U_1$$

or $$p_1v_1 + U_1 = p_2v_2 + U_2.$$

That is, in general on both sides of the plug we have the same value for the expression $(pv + U)$, or—

$$pv + U = \text{constant}.$$

If Boyle's Law $(pv)_T$ = constant and Joule's Law (U = KT) both held gold, then $pv + U$ *would depend on temperature only, i.e.* would be uninfluenced by the volume change which necessarily takes place on passing from a high to a low pressure. But $(pv + U)$ is shown to be constant *whether the gas laws are obeyed or not*, and hence, if they were obeyed, T would necessarily be a constant likewise, that is, there would

be no Joule-Thomson effect (cooling or heating) on passing through the plug. The existence of the temperature change is therefore due to one or both of the laws breaking down.

(1) *Deviation from Boyle's Law.*

This need not be gone into here, as it has already been discussed (Vol. I. chap. ii.). It may be recalled that with increase of pressure up to a certain value gases—with the exception of hydrogen—show themselves to become more compressible than the law required. In the plug experiment, therefore, we see what the effect of this will be, that the product (pv) for a given mass *is greater* on the *low*-pressure side than the corresponding product for the same mass on the high-pressure side. Here, in order that pv may become the same on both sides (since $pv + U$ is the same on both sides) it is necessary to *lower* the *temperature* on the low-pressure side, *i.e.* the gas cools on passing through the plug. Thus from the observed deviations from Boyle's Law we would expect a cooling on the lower-pressure side of the plug except in the case of hydrogen.[1] Further, we may consider the case in which the pressure is so great that for all gases (at room temperature) the compressibility is less than that of a perfect gas, *i.e.* we suppose that we are at the region of ascending curves on the ($(pv)p$) diagram. In such a case the value of pv of a given mass on the high-pressure side may be greater than that on the low-pressure side, and hence the temperature on the low-pressure side would have to be raised to bring the pv up to the value of the other side. It is conceivable, however, that the pressures might be so chosen that the pv values (as given on the Amagat diagram) are the same on both sides of the plug. This, however, would not mean that the temperature would remain the same on both sides, for the expression which must be constant is ($U + pv$), not pv alone.

(2) *Deviation from Joule's Law.*

According to Joule's Law the internal energy of a given mass should depend on the temperature and not on the volume occupied. Since in actual gases cohesive forces are present, it follows that in an expansion, work must be done in drawing the molecules apart, and therefore at the larger volume the given mass contains a greater value of U than at the smaller volume, and hence if U is to be constant on both sides of the

[1] Note that with regard to the Amagat ($(pv)p$) diagram one must be careful not to confuse the inversion point of the plug thermal effect above referred to, with the series of temperatures for which for a given p the expression pv is a minimum. (At such points it is true that Boyle's Law is momentarily obeyed, and if the plug experiment required the expression pv to be the same on both sides, then we could calculate from Amagat's ($(pv)p$) diagram what difference of pressure is required at a given temperature to cause no thermal effect. The expression which holds for both sides of the plug is, however, $pv + U$ = constant). There is no connection between the porous plug inversion point and the ($(pv)p$) diagram "inversion" points.

plug we must decrease the temperature on the larger volume side, *i.e.* in the low-pressure side. This should hold for *all* gases.

We might summarise the thermal effects to be expected on the low-pressure side of the plug owing to deviations from the Gas Laws as follows :—

Deviations from Boyle's Law.—Heating or cooling produced according to the temperature and actual absolute pressure worked at.

Deviations from Joule's Law.—Cooling in all cases. The observed phenomena will be the resultant of these simultaneous effects.

The Joule-Thomson porous plug experiment has received an important technical application in that it is the basis of one of the methods used in the liquefaction of gases. *Cf. infra.*

We may now treat the porous plug thermal phenomena from a somewhat more quantitative thermodynamic standpoint. In the first place it must be pointed out that we are dealing with an irreversible phenomenon, since we cannot make the gas retrace its path from low to high, the pressure difference being a finite one, and the heat is therefore dissipated. However, the function $(U + pv)$ depends solely on the actual state of the gas, and so its variation in value between two states depends solely on the two states and *not on the path of transformation between them*, whether that be reversible or not. Now we have already seen (page 55) that—

$$d(U + pv) = C_p dT + (l' + v)dp$$

and

$$l' = -T\left(\frac{\partial v}{\partial T}\right)_p.$$

Therefore $d(U + pv) = C_p dT + \left(v - T\left(\frac{\partial v}{\partial T}\right)_p\right)dp.$

Hence, since $U + pv$ has the same value on both sides of the plug, *i.e.* since $d(U + pv) = 0$, it follows that—

$$C_p dT + \left(v - T\left(\frac{\partial v}{\partial T}\right)_p\right)dp = 0$$

is the equation connecting the change of temperature (on passing through the plug) with the change of pressure.

This expression should hold good in all cases. Now, if we happen to be at the temperature at which there is no change of temperature, *i.e.* $\Delta t = 0$, and since dp is not zero, we have—

$$T\left(\frac{\partial v}{\partial T}\right)_p - v = 0$$

as the criterion of the inversion point, this denoting the temperature at which the thermal effect is nil. We can see, perhaps, a little more clearly the physical meaning of this expression if we divide across by v. The expression is then—

$$\frac{T}{v}\left(\frac{\partial v}{\partial T}\right)_p = 1 \quad \text{or} \quad \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{T}.$$

The coefficient of thermal expansion at constant pressure is $\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$, and hence the inversion point is defined as the temperature at which the coefficient of expansion of the fluid at constant pressure is equal to the reciprocal of the absolute temperature.

Liquefaction of Gases.

Two methods are now in use technically, namely, the free-expansion method (Hampson's and Linde's machines) and the work-expansion method (Claude's machine).

In the free expansion method the liquefaction is regarded as being entirely due to the Joule-Thomson effect. The compressed gas is allowed to escape through a fine nozzle into an expansion chamber, the cooled gas being caused to flow back over the pipe containing the oncoming compressed gas which is thus cooled progressively, until finally its temperature has fallen so low that the free expansion at the nozzle causes the formation of drops of liquid. The cooling effect produced in this way is by no means great unless high pressures are used. In the following table are given a few data upon air. Δt denotes the *lowering* in temperature produced by the expansion when the air is initially at a temperature $t°$ C., and under a pressure of p atmospheres, the gas expanding to a pressure of one atmosphere.

$t°$ C.	$p = 68$ Δt.	$p = 204$ Δt.
0	17·1	44·6
− 20	20·3	52·1
− 50	25·8	66·4
− 90	40·2	99·2

In the work expansion method the cooling is mainly due to the fact that the gas is made to do work adiabatically in driving an engine, either a turbine or piston machine. This engine driven by the expanding gas is connected to the compressor and assists the latter to compress the gas as it is fed into the machine. The cooling effect brought about as a result or doing work is much greater than that produced by the act of free expansion alone. Of course even in the work expansion method the gas cools in consequence of the Joule-Thomson effect, but this is small compared with the cooling produced by the act of working the engine adiabatically. Progressive cooling of the gas is brought about in a manner similar to that already described in connection with the free expansion method. It is perhaps rather fanciful but nevertheless correct to say that a perfect gas could be liquefied by the work expansion method, although it would not experience any Joule-Thomson effect. In the Claude machine, liquefying air, about 95 per cent of the total cooling is due to the work done, the remaining 5 per cent being due to the Joule-Thomson effect.

The Criteria of a Perfect Gas.

If there is no temperature change in the Joule-Thomson experiment, the following relation must hold:—

$$T\left(\frac{\partial v}{\partial T}\right)_p - v = 0.$$

This will be satisfied by writing—

$$v = Tf_1(p)$$

where $f_1(p)$ is an integration constant independent of T. A perfect gas will satisfy this as a special case, for a perfect gas has no plug thermal effect at any temperature. Further, if there is no change in temperature in the Joule experiment, we have (p. 52)—

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = 0.$$

This will be satisfied by the expression—

$$p = Tf_2(v)$$

where $f_2(v)$ is an integration constant independent of T. Again, a perfect gas must satisfy this as a special case. Other substances might satisfy one or other of the criteria $v = Tf_1(p)$ and $p = Tf_2(v)$, but to satisfy both the substance must be a perfect gas. For suppose we have a substance for which the relations hold good simultaneously, *viz.*:—

$$p = Tf_2(v)$$
$$v = Tf_1(p)$$

then for this substance we must have—

$$\frac{p}{v} = \frac{f_2 v}{f_1 p}$$

or

$$p = \frac{v f_2(v)}{f_1(p)}.$$

In order that the right-hand side may really be p, it is evident that $f_2 v$ must be $\frac{k}{v}$, $f_1 p$ must be $\frac{k}{p}$, k being a constant the same in both. For this substance, therefore, which satisfies the above relations, the two preceding relations take the form of—

$$\left.\begin{aligned} p &= \frac{kT}{v} \\ v &= \frac{kT}{p} \end{aligned}\right\} \textit{i.e.}\ \text{both expressions become identical, giving—}$$

$$pv = kT$$

which is the equation characteristic of a perfect gas.

The Use of "Porous Plug" Inversion Points in Testing Proposed Equations of State.[1]

The way of setting about this problem is to inquire if the equations which have been proposed for real (imperfect) gases will indicate the existence of an inversion point, if the gas be passed through a porous

[1] *Cf.* A. W. Porter, *Phil. Mag.*, series [6], p. 554, vol. 11, 1906; series [6], ol. 19, 1910.

plug. Will a gas which obeys van der Waals' expression, for example, show this behaviour?

(a) *Investigation of van der Waals' Equation.*

Instead of writing this in the usual form, it is more convenient to make use of the *reduced* form, *i.e.* pressures, volumes, and temperatures will be expressed as fractions α, β, γ of their critical values. The results will be the same for every fluid obeying this equation (*cf.* the section dealing with corresponding states (Vol. I. chap. ii.)). The reduced van der Waals equation is—

$$\left(\alpha + \frac{3}{\beta^2}\right)(3\beta - 1) = 8\gamma. \quad . \quad . \quad . \quad (1)$$

Now we have already seen that the equation characteristic of an inversion point is—

$$T\left(\frac{\partial v}{\partial T}\right)_p - v = 0$$

or, writing this in the reduced form also, we obtain—

$$\gamma\left(\frac{\partial \beta}{\partial \gamma}\right)_\alpha - \beta = 0 \quad . \quad . \quad . \quad . \quad (2)$$

By differentiating (1) with respect to β, and substituting in (2), we obtain for an inversion point the relation—

$$\frac{-8\gamma}{3\beta - 1} + \frac{6(3\beta - 1)}{\beta^2} = 0.$$

From this it follows that the inversion temperature (on the reduced scale) is given by—

$$\gamma = \frac{3(3\beta - 1)^2}{4\beta^2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From this and the previous equation, γ can be eliminated with the result—

$$\alpha = \frac{9(2\beta - 1)}{\beta^2} \quad . \quad . \quad . \quad . \quad (4)$$

This formula connects the reduced pressure and volume which correspond to an inversion point. The simplest mode of calculation is to obtain γ by equation (3) for a series of assumed values of β, and then to calculate α by means of equation (4) for the same values of β. Working in this way it is found that on the γ, α diagram (Fig. 13) the curve is roughly as shown. This means, in the first place, that for a given fluid there is a continuous series of inversion points possible (corresponding to different values of β), up to a certain temperature, above which there is no inversion; and, still more striking, there are *two* temperatures corresponding to each pressure at which inversion can occur.[1]

[1] The quantitative relations are summarised by Porter as follows:—

(1) For all pressures from zero to nine times the critical pressure there are two inversion temperatures which may range from a little below the critical temperature to about 6·7 times the critical value.

(2) At pressures higher than nine times the critical value there is no inversion point.

In the diagram (Fig. 13) the dotted curve gives the position of the inversion points as deduced from van der Waals' equation. A line drawn perpendicular to the α ordinate cuts the dotted curve at two

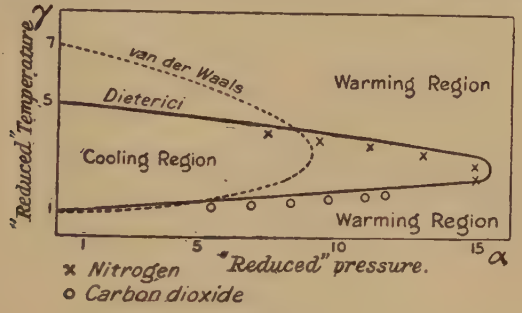


FIG. 13.

points, these points being the inversion temperatures for the given reduced pressure.

(b) *Investigation of Dieterici's Equation.*[1]

This equation, applied by Dieterici to the case of isopentane, is written—

$$p(v - b) = RTe^{\frac{-A}{RT^{3/2}v}}$$

or in the reduced form

$$\alpha(2\beta - 1) = \gamma e^{2\left[1 - \frac{1}{\beta\gamma^{3/2}}\right]}.$$

The inversion points corresponding to this equation are given by the relation—

$$\alpha\gamma^{\frac{1}{2}} = (10 - \gamma^{\frac{3}{2}})e^{2\left[1.2 - \frac{2}{\gamma^{3/2}}\right]}.$$

This also gives a curve for inversion points, which is shown as a full line in the diagram already referred to. The curve obtained by Dieterici's and van der Waals' equations respectively are of the same type, but at the same time they differ so markedly that it should be possible to discriminate between them as regards their validity on comparing the results with those based on experimental data. Unfortunately such data are very scanty. Porter (*loc. cit.*) has calculated some inversion points in the case of nitrogen as far as Amagat's data permitted. A similar calculation was carried out in the case of carbon dioxide. In the diagram the experimental points for nitrogen are denoted by crosses, those for carbon dioxide being denoted by circles. In neither case are there sufficient data available to permit the following of the theoretical curve over a wide range. In the case of nitrogen,

[1] Dieterici's equation has recently been examined in a thorough manner by F. H. McDougall (*J. Amer. Chem. Soc.*, 38, 528, 1916).

however, the turning point indicating the highest temperature at which inversion is possible is clearly seen. It is important to note that while the values for nitrogen lie on the upper part of the curve, those for carbon dioxide lie on the lower part. A glance at the diagram is sufficient to show how much better Dieterici's equation reproduces the experimental values than does van der Waals' equation. On the basis of the porous plug experiment the conclusion is, therefore, that Dieterici's equation is more in agreement with the observed behaviour of fluids than is van der Waals'.

The problem of the shape of the curves indicated in Fig. 13 has been investigated by A. Daniell (*private communication*), who finds that the curves are not true parabolas and not symmetrical. Daniell further points out that the Dieterici curve, so far as it is given in the diagram, starts at the origin of the axes and remains very close to the γ axis from $\gamma = 0$ to $\gamma = 1$; the curve then turns off sharply in an almost horizontal direction as shown in the figure. Instead therefore of the Dieterici curve cutting the γ axis at $\gamma = 1$, the reader is to imagine it as almost reaching the axis at this value and then dropping almost perpendicularly to $\gamma = 0$.

Heterogeneous Systems consisting of Saturated Vapour in Contact with Liquid.

The Equality of the Segments of the Hypothetical Isotherm in the Heterogeneous Region.

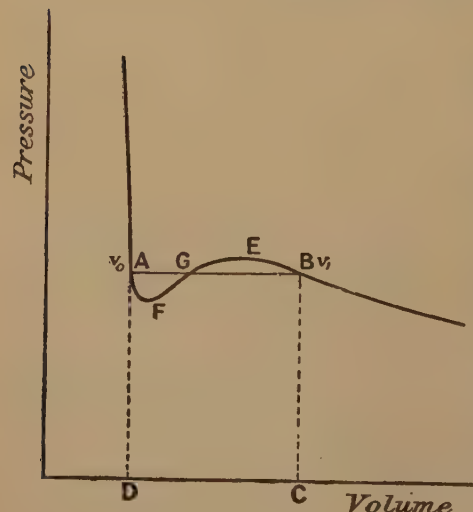


Fig. 14.

According to the Second Law of Thermodynamics the external work done by a system in passing isothermally and reversibly from the initial to the final stage is independent of the path followed. Let us apply this principle to the consideration of the passage from the completely gaseous (volume v_1) to the completely liquid state (volume v_0), this change being supposed to take place isothermally. Referring to the pv diagram (Fig. 14) already given, it is evident if we consider the region of saturation that we can pass from v_1 to v_0 by either of two ways; namely, along the horizontal constant pressure line, which is the actual passage

followed by the system, or on the other hand, by the hypothetical isotherm suggested by James Thomson, and reproducing the van der Waals equation. Following the first path, namely, the horizontal AB, the external work done in compressing is represented by the expression $p(v_1 - v_0)$, where p is the vapour pressure. This work is represented by the area ABCD. Following the second path, namely BEGFA, the work done is $\int_{v_1}^{v_0} p\,dv$, where p is no longer constant but varies continually throughout the volume change. This work term is represented in the diagram (Fig. 14) by the area BEGFADC, and it is evident that if BEGFADC is equal to ABCD, it follows that the two areas BEG and GFA are equal, that is :—

$$p(v_1 - v_0) = \int_{v_0}^{v_1} p\,dv.$$

This was first pointed out by Maxwell. The conclusion is probably correct, but it must not be forgotten that the second path followed is a hypothetical one never yet realised in practice—at least between E and F.

The Method of applying van der Waals' Equation to the Heterogeneous System, Vapour-Liquid.

It has been already pointed out that van der Waals' equation applies, *i.e.* reproduces experimental facts at least approximately, for the homogeneous system consisting *either* of liquid *or* of gas. By the introduction of the Maxwell assumption considered above, it is possible to use van der Waals' equation, to obtain information regarding pressures and volumes of heterogeneous systems in the following way. The two points A and B both lie on the hypothetical and the real isotherms. To each of these points we can apply the van der Waals equation. Further, the points A and B represent the values which are the limits of integration in the expression $\int_{v_0}^{v_1} p\,dv$. We can therefore apply van der Waals' equation to carry out this integration by writing p as a function of v, namely—

$$p = \frac{RT}{v - b} - \frac{a}{v^2}.$$

Hence
$$\int_{v_0}^{v_1} p\,dv = RT \log \frac{v_1 - b}{v_0 - b} + \frac{a}{v_1} - \frac{a}{v_0}$$

a and b being regarded as constants.

But according to Maxwell's assumption—

$$\int p\,dv = p(v_1 - v_0).$$

$$\therefore p(v_1 - v_0) = RT \log \frac{v_1 - b}{v_0 - b} + \frac{a}{v_1} - \frac{a}{v_0}$$

$$\left(p + \frac{a}{v_1 v_0}\right)(v_1 - v_0) = RT \log \frac{v_1 - b}{v_0 - b} \quad . \quad . \quad (1)$$

The point A is characterised by the equation—

$$\left(p + \frac{a}{v_0^2}\right)(v_0 - b) = RT \quad . \quad . \quad . \quad (2)$$

The point B is characterised by—

$$\left(p + \frac{a}{v_1^2}\right)(v_1 - b) = RT \quad . \quad . \quad . \quad (3)$$

From these three equations it is possible to find, for example, vapour pressures or specific volumes of liquid and of saturated vapour as functions of the temperature.

Expressions for the Pressure of Saturated Vapour (in contact with Liquid) and the Heat of Vaporisation.

In the section dealing with the continuity of state from the kinetic standpoint, we have considered several expressions of this kind in some detail (Vol. I. chap. ii.). The problem still deserves a little further discussion. The most important relation between latent heat of vaporisation and pressure is that deduced on the basis of the First and Second Laws of Thermodynamics, and known as the Clapeyron equation, which may be written, on the assumption that the vapour obeys the gas laws, in the form—

$$\lambda_m = RT^2 \frac{d \log p}{dT}$$

in which λ_m represents the molecular heat of vaporisation, R having the value 1·985 calories. This can be rewritten in terms of the concentration C of the saturated vapour by applying the gas law in the form $p = CRT$, namely—

$$\lambda_m - RT = RT^2 \frac{d \log C}{dT}.$$

The left-hand expression denotes the internal molecular latent heat of vaporisation. As measurements show this heat varies in a continuous and gradual manner with temperature; we can therefore write—

$$\lambda_m - RT = \lambda_0 + \alpha_0 T + \beta_0 T^2 + \gamma_0 T^3 + \text{etc.}$$

Employing this to integrate the above equation, one obtains—

$$\log C = \frac{-\lambda_0}{RT} + \frac{\alpha_0}{R} \log T + \frac{\beta_0}{R} T + \frac{\gamma_0}{2R} T^2 + \ldots + i$$

where i is an integration constant. We can easily transform this back into vapour pressure terms by putting $p = RTC$, whereby we obtain—

$$\log p = \frac{-\lambda_0}{RT} + \frac{(\alpha_0 + R)}{R} \log T + \frac{\beta_0}{R} T + \frac{\gamma_0}{2R} T^2 + \ldots + i + \log R.$$

The last two terms may be added and considered as a single constant—

$$C_0 = \frac{i + \log R}{2{\cdot}3023}.$$

This term C_0 is called by Nernst (*Applications of Thermodynamics to Chemistry*) "the chemical constant" of the substance in question. It must be remembered that at ordinary temperatures the gas laws only hold approximately for saturated vapour. At lower temperatures, however, the application of the gas laws becomes increasingly more valid. For this reason, therefore, Nernst and his pupils have in recent years carried out a considerable number of very accurate vapour pressure determinations at temperatures considerably below 0° C. Details of these will be found in his book already referred to (*Applications of Thermodynamics to Chemistry*), and also J. T. Barker (*Zeit. für physik. Chem.*, **71**, 235, 1910).

The calculation of i or C_0 can be of course carried out directly by substituting a number of experimentally determined values for $\log p$ in the vapour pressure equation given above. Nernst has, however, modified this form of procedure in several ways. It would be, however, outside the scope of this book to go further into this point. Full details are given in Nernst's *Applications of Thermodynamics to Chemistry*. The following table contains a summary of the values of the chemical constant $\frac{i + \log R}{2{\cdot}3023}$ (Nernst, *loc. cit.*, p. 75):—

Substance.	Chemical Constant per Mole.	Substance.	Chemical Constant per Mole.
Hydrogen	2·2[1]	Carbon-dioxide	3·2
Methane	2·5	Carbon-bisulphide	3·1
Nitrogen	2·6	Ammonia	3·3
Oxygen	2·8	Water	3·7 (3·6)
Carbon-monoxide	3·6	Carbon-tetrachloride	3·1
Chlorine	3·0	Chloroform	3·2
Iodine	4·0	Benzene	3·1
Hydrochloric acid	3·0	Ethyl alcohol	4·1
Nitric oxide	app. 3·7	Ether	3·3
Nitrous oxide	3·3	Acetone	3·7
Sulphuretted hydrogen	3·0	Propyl acetate	3·8
Sulphur-dioxide	3·3		

As a general rule the value of the chemical constant is about 3.

Another interesting relation is that known as *Trouton's Law*. According to this law the molecular latent heat of vaporisation divided by the boiling point[2] is a constant. The limits of applicability will be seen from the following table (Louguinine's data, *Winkelmann's Handbuch*, vol. iii.):—

[1] Nernst's Text-book, English translation of the 6th German edition, gives $C_0 = 1{\cdot}6$ for H_2.

[2] In absolute units.

Substance.	Boiling Point.	$\frac{M\lambda}{T}$.
Methyl ethyl acetone	78·68° C.	21·25
Diethyl acetone	101·08	20·90
Dipropyl acetone	143·52	20·73
Acetal	102·91	20·78
Octane	125·3	20·28
Aniline	184·24	21·22
O. Toluidine	198·92	21·55
Nitro-benzene	210·6	20·70
Acetonitrile	81·54	19·74
Pyridine	115·51	20·12
Ethyl alcohol	78·20	26·39
n.-Propyl alcohol	96·1	26·59
iso-Butyl alcohol	107·53	26·12
Acetic acid	119·2	13·74
Propionic acid	141·05	16·34

The "normal" value for the constant is about 20·7, and a large number of different substances approximate fairly closely to this. On the other hand, substances such as the alcohols and acids, which are known to be polymerised in the liquid state, give different values for the constant. The law therefore is not general.[1] Although put forward in the first instance as an empirical relation, it has a certain amount of theoretical basis from the standpoint of van der Waals' theory of corresponding states. The reasoning is as follows:—

Starting from the Clapeyron equation—

$$\lambda = T\frac{dp}{dt}(v_1 - v_0)$$

and rewriting the T, p, and v terms in reduced units—

$$\alpha = \frac{p}{p_c};\ \beta = \frac{v}{v_c};\ \gamma = \frac{T}{T_c}$$

this expression becomes—

$$\frac{\lambda}{T} = \frac{p_c v_c}{T_c}\frac{d\alpha}{d\gamma}(\beta_1 - \beta).$$

Now if we consider one gram-mole of each of a series of substances the molecular latent heat becomes $M\lambda$. Since we are dealing with the same number of molecules in all cases, R is the same, and the expression $\frac{p_c v_c}{T_c}$ will be the same for all (namely, $\frac{R}{2\cdot67}$ according to van

[1] A modified form of Trouton's expression has been suggested by Hildebrand, *cf.* Smith and Calvert, *J. Amer. Chem. Soc.*, 38, 1916.

der Waals' equation, or $\frac{R}{3{\cdot}75}$ in actual cases). Further, if we are comparing the substances at corresponding temperatures, α, β, and γ will be the same for all substances, and therefore at *corresponding temperatures* the expression $\frac{M\lambda}{T}$ will be the same for all substances. Now Guldberg (*Zeitsch. physik. Chem.*, **5**, 374, 1890) and Guye (*Bull. Soc. Chim.*, **4**, 262, 1890) have pointed out that the ordinary boiling points of liquids—under atmospheric pressure—are practically corresponding temperatures; the boiling points being approximately two-thirds of the critical temperature *i.e.* $\gamma = \frac{2}{3}$. Hence at the boiling point $\frac{M\lambda}{T}$ should be constant for all substances. This is Trouton's Law.

A further semi-empiric expression for $M\lambda$ [1] has been given (Nernst, *Applications of Thermodynamics to Chemistry*, p. 103, or *Theoretical Chemistry*, English translation, 6th German edition, p. 273), namely—

$$M\lambda = R\frac{T_1T_2}{T_1 - T_2}\left(1 - \frac{p}{p_c}\right)\log\frac{p_1}{p_2}$$

in which p_1 and p_2 denote vapour pressures corresponding to T_1 and T_2, two temperatures which differ by so small an amount that their geometrical and arithmetical means may for practical purposes be said to equal one another. This mean temperature is the one to which λ corresponds. This formula gives in fact values which agree with the direct measurements; in general the heats of vaporisation calculated with its aid are more accurate than those determined calorimetrically. In the following table are given the values of the boiling point T_0 (on absolute scale), and molecular latent heat of vaporisation calculated by the above expression; with the exception of the case of hydrogen, where Dewar's experimental value is employed. The third column gives the value of $\frac{M\lambda}{T_0}$, which is Trouton's expression. It will be seen that this value is by no means constant:—

Substance.	T_0.	$M\lambda$ in Calories.	$\frac{M\lambda}{T_0}$.	$9{\cdot}5 \log T_0 - 0{\cdot}007\, T_0$.
Hydrogen	20·40	248	12·2	12·3
Nitrogen	77·5	1362	17·6	17·4
Air	86·0	1460	17·0	17·8
Oxygen	90·6	1664	18·3	18·0
Ether	307	6466	21·1	21·5
Carbon bisulphide . .	319	6490	20·4	21·6
Benzene	353	7497	21·2	21·7

The expression occurring in the last column is given by Nernst, who

[1] Nernst uses λ to denote molecular latent heat. We have used it to denote latent heat per gram.

calls it the revised rule of Trouton, *i.e.* the expression $\frac{M\lambda}{T_b}$ is not to be regarded as a constant, but as a function of the temperature according to the relation—

$$\frac{M\lambda}{T_0} = k_1 \log T_0 - k_2 T$$

where k_1 and k_2 are 9·5 and 0·007 respectively for all substances. In this case, however, the polymerised substances do not show agreement. The further relations connected with the pressures of saturated vapours will be taken up later from the standpoint of Nernst's Third Law of Thermodynamics.

Bakker's Equation.

In 1888 (*Dissertation*, Scheidam) G. Bakker put forward the following relation—

$$\lambda = \int_{v_0}^{v_1} K dv + p(v_1 - v_0)$$

where K = internal pressure or cohesive force per unit area across any section in the interior of the fluid. $K dv$ represents therefore the *internal* work done when the system expands by dv.

λ = latent heat of vaporisation per gram.
v_1 = volume of 1 gram of vapour
v_0 = volume of 1 gram of liquid
} at the same temperature.
p = vapour pressure.

We may write this expression in the approximate form—

$$\lambda = \int_{v_0}^{v_1} K dv + \frac{RT}{M}$$

in which we have neglected v_0 compared to v_1 and have put $pv_1 = \frac{RT}{M}$ as a first approximation (M = molecular weight of vapour).

Or calling λ_i the internal latent heat per gram—

$$\lambda_i = \int_{v_0}^{v_1} K dv.$$

Bakker integrated this expression on the assumption that K may be represented as a function of v, according to the expression $K = \frac{A}{v^2}$, where A is a constant. This leads to the equation—

$$\lambda_i = A\left(\frac{1}{v_0} - \frac{1}{v_1}\right), \text{ or approximately } \frac{A}{v_0}.$$

It may be noted that Bakker deduced this expression without reference to van der Waals' equation. In van der Waals' equation $K = \frac{a}{v_2}$,

so that the A in Bakker's equation would become identical with a provided K were really represented by $\frac{a}{v_2}$, *that is provided a were independent of temperature.* Bakker himself (*Zeitsch. physik. Chem.*, **12**, 670, 1893) has shown the connection between A and a namely—

$$A = \left(a - T\frac{\partial a}{\partial T}\right).$$

Let us, however, regard a as independent of temperature, as a first approximation. Call it a_t at the temperature of the vaporisation considered. To illustrate how far Bakker's relation in the form—

$$\lambda = \frac{a_t}{v_0} + \frac{RT}{M}$$

applies in practice, a table due to J. Traube (*Annalen der Physik*, [4], **8**, 300, 1902), is given below. It will be observed that a_c (the value of van der Waals' constant at the critical temperature) is greater than a_t (the value of the same "constant" at the temperature of vaporisation), and hence Traube gives two series of calculated values for the latent heat. The a_t values were obtained by Traube from the abbreviated van der Waals equation—

$$\frac{a}{v}(v - b) = RT.$$

Substance.	T − 273.	b_t in c.c.	v_0 in c.c.	a_c in Liter² Atmosp.	a_t in Liter² Atmosp.	λ Calc. I. Using a_c.	λ Calc. II. Using a_t.	λ Observed in Cal. per Gram-molecule.
Mercury . . .	360·0	14·2	15·72	—	8·68	—	14,660	14,540[1]
Iso-pentane . .	28·0	87·3	117·9	18·20	11·23	4,340	2,910	6,000
n.-Hexane . .	69·0	104·1	139·8	24·58	15·37	—	3,340	—
Ethyl ether . .	34·8	79·3	106·4	17·44	10·56	4,590	3,020	6,260
Chloroform . .	60·9	—	84·5	14·71	—	4,880	—	6,985
Carbon tetra-chloride	76·2	78·1	103·7	19·20	12·04	5,185	3,510	7,130
Carbon bisulphide .	46·2	—	62·1	11·20	—	5,010	—	6,600
Benzene . . .	80·25	72·1	96·2	18·36	11·13	5,050	3,510	7,290
Methyl formate .	32·9	47·6	62·7	11·38	6·54	5,010	3,140	6,970
Ethyl acetate . .	75·9	78·7	106·0	20·47	11·79	5,380	3,390	7,640
Nitrogen . . .	−194·4	—	33·2	1·35	—	1,140	—	1,620
Sulphur dioxide .	10·0	—	43·9	6·61	—	4,175	—	6,090
Ethyl alcohol . .	78·1	—	62·3	15·22	—	6,620	—	9,440
Acetic acid . .	119·2	48·0	63·8	17·60	8·29	5,390	3,930	7,470
Water . . .	100	15·5	18·9	5·77	3·29	8,190	4,980	9,660

[1] This is not the figure given by Traube in 1902, but the later value given by him in *Zeit. f. anorg. Chem.*, **34**, 423, 1903.

The term a is given in (liter)² × atmosphere because $\frac{a}{v^2}$ has the dimensions of a pressure, and therefore $\frac{a}{v}$ is energy, so that a = energy × volume.

Traube made use of the values of b_t (*loc. cit.*, p. 284; *ibid.*, **5**, 552, 9101) obtained from the van der Waals equation at two slightly different temperatures in the region required. The values of a_c are those calculated by Guye (*Arch. Science phys. et natur.*, *Genève*, **9**, 22, 1900)—

$$a_c = \frac{27}{64}\frac{R^2T_c^2}{P_c}.$$

The column headed λ calc. I. refers to a_c; λ calc. II. refers to a_t. It may be pointed out that the term a_c has a much more definite significance than a_t since the former is obtained from the critical values of P and T alone, whilst the latter depends on the more or less arbitrary value of b_t which holds good for a certain temperature arbitrarily chosen. The values of a_t are therefore not as comparable with one another as the a_c values.

It will be noted that the agreement between observed and calculated values is not good, the observed values being greater than the calculated, and rather remarkably, the discrepancy is greater in the case of the a_t values than in those calculated from the a_c values. Traube discusses these discrepancies, but it would be outside our present purpose to follow him further. It may be noted that in the case of mercury the value of λ calculated from a_t agrees well with the observed value, thus pointing to the possibility that in the case of this substance the constant a is in reality very nearly independent of temperature. The same is approximately true for bromine, given in a later paper by Traube, *loc. cit.*, namely, λ observed, 7296 calories; calculated, 6620 calories, The same thing holds good for zinc and cadmium (and perhaps for other metals as well), *viz.* :—

	λ Observed per Gram-molecule.	$\frac{a_t}{v} + RT$.[1]
Zinc . . .	25,500	25,450
Cadmium . .	23,480	23,450

For sulphur, however, the discrepancy is marked: λ observed, 23,170 calories per gram-molecule; $\frac{a_t}{v} + RT = 32{,}300$ calories. It may be noted that in Traube's table of liquid substances already given, water and the alcohols which are known to be considerably associated do not appear to behave in any characteristic manner different from other liquids as regards the values of λ calculated and λ observed. This is rather surprising.

Bakker's equation $\lambda = \frac{a}{v_0} + \frac{RT}{M}$ may be put into an alternative form

[1] Traube [*Zeit. f. anorg. Chem.*, *loc. cit.*].

by substituting an expression containing b by the aid of van der Waals' equation. Thus, according to van der Waal's equation, since $\frac{a}{v^2}$ is simply K, the cohesive pressure,

$$K = \frac{R'T}{v - b} - p$$

where R′ refers to 1 gram and may be written $\frac{R}{M}$, R being 1·985 cals.

$$\therefore K dv = \frac{R'T}{v - b} dv - p dv$$

hence
$$\int_{v_0}^{v_1} K dv = R'T \log \frac{v_1 - b}{v_0 - b} - p(v_1 - v_0).$$

Now
$$\lambda = \int_{v_0}^{v_1} K dv + p(v_1 - v_0).$$

$$\therefore \lambda = \frac{RT}{M} \log \frac{v_1 - b}{v_0 - b}.$$

b is, of course, here assumed to be a constant, and this expression is simply an equivalent of $\frac{a}{v_0} + \frac{RT}{M}$. As already pointed out, the calculated values are in nearly all cases lower than the observed, and there is no doubt that the discrepancy is due to the variation of a and b with temperature and volume.

For a discussion of the internal pressure K, *cf.* W. C. McC. Lewis, *Trans. Farad. Soc.*, **7**, part I. (1911). Also for a comparison of Bakker's expression with those of Milner, *cf.* W. C. McC. Lewis, *Zeit. f. phys. Chem.*, **79**, 196 (1912).

Dieterici's Expression for the Latent Heat of Vaporisation.

The following empirical relation for the internal latent heat of vaporisation λ_i has been found by Dieterici (*Ann. der. Physik.*, **25**, 269, 1908; *ibid.*, **35**, 220, 1911) to hold good, *viz.*:—

$$\lambda_i = CRT \log \frac{v_2}{v_1}$$

where C is a constant, v_2 and v_1 are the specific volumes of the saturated vapour and liquid respectively, and R refers to 1 gram. The constancy of C is shown by the following results based on S. Young's data for iso-pentane—

Iso-pentane (t_c = 187·8° C.; T = 460·8); p_c = 25,010 mm. of mercury, v_c = 4·266 c.c.:—

T abs.	Pressure of Saturated Vapour.	v_1.	v_2.	λ_i Obtained from Clapeyron Equation.	$R T \lg \frac{v_2}{v_1}$	C.
283·0	390·5	1·5885	607·5	78·64 calories	46·15	1·704
293·0	572·6	1·6141	424·0	75·97 ,,	44·76	1·697
303·0	815·3	1·6413	303·0	73·52 ,,	43·35	1·696
323·0	1533·0	1·7005	167·6	68·95 ,,	40·66	1·696
343·0	2653·0	1·7679	98·9	64·18 ,,	37·86	1·695
363·0	4296·0	1·8475	61·85	59·49 ,,	34·94	1·703
383·0	6596·0	1·9455	39·80	53·78 ,,	31·71	1·696
403·0	9707·0	2·0720	26·10	47·65 ,,	27·99	1·702
423·0	13804·0	2·2500	17·14	40·18 ,,	23·56	1·705
443·0	19094·0	2·5550	10·71	29·53 ,,	17·40	1·697
458 0	23992·0	3·1830	6·355	14·17 ,,	8·68	1·632
460·8	25010·0	4·266	4·266	0	0	—

It will be seen that the constant C is really an excellent constant for low temperatures up to the neighbourhood of the critical point. That the above expression, involving the expressions v_1 and v_2, should hold good is very surprising; one would have expected that the "b" correction should have been brought in, giving an expression containing $\log \frac{v_2 - b_2}{v_1 - b_1}$, but this does not give C a constant, unless we assume that $\frac{b_1}{b_2} = \frac{v_1}{v_2}$, which is known to be not the case. Not only do we obtain a value for C which is independent of the temperature for a single substance such as iso-pentane, it is also found that this value for C is approximately a general constant holding for all normal—non-associated—substances, as the following table shows. The value for C for each substance is the *mean* value obtained from a wide temperature range similar to the iso-pentane case. Dieterici states that the variation in C for each substance is not more than 2 per cent. :—

Substance.	C.	Substance.	C.
n.-Pentane	1·707	Zinc chloride	1·741
n.-Hexane	1·752	Ethyl ether	1·724
n.-Heptane	1·814	Methyl formate	1·706
n.-Octane	1·858	Ethyl formate	1·747
2 : 3 dimethyl n.-Butane	1·725	Methyl acetate	1·784
di-iso-butyl or 2 : 5 dimethyl n.-hexane	1·813	Propyl formate	1·774
		Ethyl acetate	1·812
Hexamethylene	1·694	Methyl propionate	1·803
Benzene	1·690	Propyl acetate	1·850
Fluor-benzene	1·711	Ethyl propionate	1·837
Chlor-benzene	1·714	Methyl butyrate	1·824
Brom-benzene	1·691	Methyl iso-butyrate	1·810
Iodo-benzene	1·687	Carbon dioxide	1·717
Carbon-tetrachloride	1·667	Sulphur dioxide	1·730

The reader must be careful not to confuse C with C_0 (Nernst's "Chemical Constant") already referred to.

The alcohols and acetic acid do not give a constant independent of temperature.

If we were dealing with a perfect gas and allowed it to expand from volume v_1 to volume v_2, the work done would be $RT \log \frac{v_2}{v_1}$. The expression for the internal energy change involved in the vaporisation, namely $CRT \log \frac{v_2}{v_1}$, has a formal resemblance to this, but it must be remembered that this latter expression only holds for singular points at each temperature, namely, the volumes of the saturated vapour and the liquid respectively. It does not follow that the energy difference will be C times the ideal work done in general for *any* volume change in a liquid system. v_1 and v_2 must only represent the limits above named. Dieterici makes use of the above considerations to show that any equation of state, *e.g.* van der Waals', which assumes that pressure is only due to translatory motion of the particles, and not in any way connected with internal motion—perhaps rotational—is necessarily incomplete. (*Cf.* Dieterici, *Annal. der Physik*, **35**, 229, 1911).

The Thermal Properties of Saturated Water Vapour (*Steam*).

Let us consider 1 gram of H_2O consisting of $(1 - m)$ grams of liquid and m grams of steam in contact. The water may be considered either as carried along with the steam, producing "wet steam," or as a two-layer system, liquid and vapour. (When $m = 1$, the system has become entirely dry saturated steam.) At a given temperature, let the volume of 1 gram of water be v_0, and the volume of 1 gram of steam, v_1. The total volume of the system V is given by—

$$V = (1 - m)v_0 + mv_1.$$

Now, suppose a small quantity of heat dQ is added to the system. In consequence there will be (*a*) a rise in temperature, (*b*) further evaporation, for since the vapour remains saturated, the higher the temperature the greater the quantity (mass) of water is required to saturate a given volume. Suppose a mass dm of water has been turned into steam. Heat required $= L dm$. Also, if at the same time the temperature has risen $dT°$, we have warmed up m grams of steam and $(1 - m)$ grams of water through this temperature, the heat required being—

$$ms_2 dT + (1 - m)s_1 dT$$

where s_1 = specific heat of water, s_2 = specific heat of saturated steam, *i.e.* the heat required to turn 1 gram of steam saturated at T_0 into saturated steam at $T_0 + 1$. s_2 *may be negative*, and is negative for steam at not too high temperatures. This remarkable phenomenon of a negative specific heat depends essentially on the fact that a given volume at 101° C., say, can contain a greater mass of saturated steam than it can contain at 100° C. One gram of steam occupies a certain

volume at 100° C. *when saturated.* At 101° C. the same mass would occupy a smaller volume in order to keep itself saturated. Hence, if we take some steam, saturate it at 100° C., and adiabatically compress it (*i.e.* the same mass) to the smaller volume which it will occupy if saturated at 101° C., we find that the heat of compression has now raised the steam above 101° C., and we have actually to withdraw heat from it. That is to say, to raise 1 gram of steam 1° C., we have to remove heat, *i.e.* s_2 is negative. Again, take a certain mass of saturated steam at 100° C., suppose we desire to lower its temperature to 99° C., still keeping it saturated. We can accomplish this by adiabatically expanding it up to the volume which it would occupy if saturated at 99° C. On doing this, it will be found to be actually at a lower temperature than 99° C. Heat would therefore have to be added to bring it to 99° C. Again, this means that s_2 is negative.

The Change of the Specific Heat of Saturated Vapour with Temperature.

Let s_1 and s_2 refer to any saturated liquid and vapour, not necessarily water.

As before, add the quantity of heat dQ. Then we can write—

$$d\mathrm{Q} = \mathrm{L}dm + (ms_2 + (1 - m)s_1)d\mathrm{T}.$$

If we divide dQ by the temperature at which it was added, we obtain $\frac{d\mathrm{Q}}{\mathrm{T}}$ or dS. The increase in entropy of the system is given by—

$$\frac{\mathrm{L}dm}{\mathrm{T}} + (s_2m + (1 - m)s_1)\frac{d\mathrm{T}}{\mathrm{T}}.$$

Now, since dS is a complete differential, we can apply the mathematical operation to which we have already referred in such cases, and which takes the form—

$$\frac{\partial}{\partial m}\left(\frac{s_2m + (1 - m)s_1}{\mathrm{T}}\right) = \frac{\partial}{\partial \mathrm{T}}\left(\frac{\mathrm{L}}{\mathrm{T}}\right)$$

whence

$$\frac{s_2 - s_1}{\mathrm{T}} = \frac{\partial}{\partial \mathrm{T}}\left(\frac{\mathrm{L}}{\mathrm{T}}\right),$$

or

$$s_2 = s_1 + \mathrm{T}\frac{\partial}{\partial \mathrm{T}}\left(\frac{\mathrm{L}}{\mathrm{T}}\right) = s_1 + \frac{\partial \mathrm{L}}{\partial \mathrm{T}} - \frac{\mathrm{L}}{\mathrm{T}}$$

s_2 will be negative when $\frac{\mathrm{L}}{\mathrm{T}} > s_1 + \frac{\partial \mathrm{L}}{\partial \mathrm{T}}$.

s_2 is found to be negative for most fluids at fairly low temperatures. Further, it is known by experience that L decreases as T increases, so that $\frac{\partial \mathrm{L}}{\partial \mathrm{T}}$ is a negative quantity. Now consider the case in which the critical temperature is reached, L = 0, since there is no difference between liquid and vapour. Hence $\frac{\mathrm{L}}{\mathrm{T}} = 0$, and since $\frac{\partial \mathrm{L}}{\partial \mathrm{T}}$ was a negative quantity up to this point, it now becomes $-\infty$. Therefore s_2 *at the*

critical point is negative and infinite. Before reaching the critical point, T has, of course, become larger so that $\frac{L}{T}$ is small, and since $\frac{\partial L}{\partial T}$ is never a numerically large quantity (below the critical point), it is reasonable to expect in many cases that—

$$s_1 > \frac{\partial L}{\partial T} - \frac{L}{T},$$

and since s_1 is always positive, s_2 *becomes positive.* s_2 thus may become positive some distance below the critical point. Since it is negative at ordinary temperatures it must pass through a stage at which it is zero.

The possible changes in s_2 with temperature can be represented in the following scheme:—

At low temperatures . . .	s_2 is negative.
At higher temperature . . .	s_2 is zero.
At still higher temperatures . .	s_2 is positive.
At the critical temperature . .	s_2 is negative and infinite.

The variations of s_2 with temperature have been investigated recently by Sir J. A. Ewing (*Phil. Mag.*, **39**, 633, 1920), and also by A. W. Porter (*ibid.*, **40**, 211, 1920). Ewing shows that in the case of ether, chloroform, benzene, and many of the esters of fatty acids, the behaviour of s_2 is as indicated in the scheme given above. Thus, in the case of ether, the specific heat of the saturated vapour is negative below 20° C. becoming zero at that temperature and then remaining positive between 20° and about 150° C. finally becoming negative as the critical point (193·8°) is approached.

Porter (*loc. cit.*) points out that sulphur dioxide also belongs to this type. He quotes a table from the data obtained by Mathias (*Comptes. Rendus*, **99**, p. 849) of which the following is an abbreviated form:—

Specific Heat of Saturated SO_2 *Vapour.*

$t°$ C.	s_2	$t°$ C.	s_2
0	− 0·410	110	+ 0·062
40	− 0·300	[114	zero]
60	− 0·235	120	− 0·078
80	− 0·165	130	− 0·306
90	− 0·095	140	− 0·620
[97·5	zero]	150	− 1·253
100	+ 0·027	155	− 3·850

On the other hand in the case of steam, alcohol, carbon bisulphide, as well as in the case of fluids commonly used in refrigerating machines, etc., carbon dioxide and ammonia, the behaviour is different. In these latter cases the specific heat of the saturated vapour remains negative throughout the whole range of temperature up to the critical point, at which point its negative value becomes infinite.

CHAPTER IV.

Thermodynamic criteria of chemical equilibrium in general.

Thermodynamic Criteria of Chemical Equilibrium.

In the consideration of Chemical Equilibrium from the Kinetic standpoint we saw that equilibrium could be conveniently divided into two classes:—

(1) Equilibrium in homogeneous systems, *i.e.* equilibrium between components in one and the same phase.

(2) Equilibrium in heterogeneous systems, *i.e.* equilibrium between components in different phases.

From the kinetic standpoint we were able to grasp the important idea involved in the term "Active Mass," and we saw how this idea led, in the case of homogeneous systems, to the generalisation known as the Law of Mass Action; and in the case of heterogeneous systems to the generalisation called the Law of Partition or Distribution.

From the standpoint of thermodynamics we can use the same division of equilibrium into the two classes, homogeneous and heterogeneous. As we shall see, we can arrive at the Law of Mass Action (without introducing the molecular hypothesis) as the criterion for homogeneous equilibrium under certain conditions; and, further, with the help of thermodynamical reasoning in the case of heterogeneous equilibrium, we arrive at a much wider principle, in addition to the Distribution Law, namely, the so-called Phase Rule. We shall study these in turn later on. For the present, however, it is necessary to consider the general problem of equilibrium.

First of all a few typical instances of physical and chemical equilibrium may be mentioned. The simplest type of equilibrium is that represented by a liquid in contact with saturated vapour in an enclosed vessel. The system will remain in an unchanged state for infinite time, the "reaction" in this case, which has reached an equilibrium, is the transfer of molecules from the liquid to the vapour and *vice versa*. This happens to be an instance of heterogeneous equilibrium. As an illustration of homogeneous equilibrium we can take the case of gaseous hydriodic acid in a state of partial dissociation into hydrogen (H_2) and iodine (I_2), or gaseous water in equilibrium with hydrogen and oxygen; or we can take the case of the equilibrium reached when acetic acid and ethyl alcohol are mixed together producing some ethyl acetate and water, all four substances being present together at certain concentration values,

in the equilibrium state; or the equilibrium which is reached when water is added to sulphuric acid, giving rise to some addition compound, thus—

$$(H_2SO_4)(H_2O)_n \rightleftarrows nH_2O + H_2SO_4$$

or, finally, we can take the case of an electrolyte dissociating in an ionising solvent, equilibrium being established (practically instantaneously) between the unionised molecules of the solute and the ions. When we come to consider any system in which a reaction may occur such a system will always tend to reach an equilibrium state. Some systems never do reach a true equilibrium state. They are under all conditions meta-stable. This, however, is due to the *slowness* of the rate at which they are progressing towards the equilibrium. Such systems give rise to an apparent equilibrium state or false equilibrium. These, however, need not concern us further here, for thermodynamics has nothing quantitative to say to such cases. We are here only considering reactions of any kind whatsoever which do within a measurable time reach the permanent state of equilibrium. The *time* criterion of equilibrium is, of course, that the system remains unchanged for infinite time. This, although true, cannot help us from the theoretical standpoint, for, of course, we cannot observe any system for infinite time. It has, however, a very *practical* use as an approximation. We are at present trying to find out thermodynamic criteria which must be satisfied when a system has come into the true equilibrium state. Let us pause to consider the conditioning factors, or, as they are called, the parameters or "variables," by altering any of which a system may in general be altered, *i.e.* the factors which determine whether a reaction will proceed or not. These factors may be large in number—temperature, pressure, concentration, electric state, capillary state, magnetic state, etc. Take a system depending on the first three of these factors, as is frequently the case, namely, the temperature, pressure, and concentration of the reacting substances. Any equilibrium may be regarded as *depending* on these factors. These three factors are, however, not all independent of one another. Suppose we take the simplest case of a gas enclosed in a vessel. We take a certain mass of gas and the vessel has a certain volume. That is, we chose the system at a certain arbitrary concentration. This system can exist as such, *i.e.* as a gas at various temperatures and various pressures. Experience shows, however, that if we arbitrarily select a definite temperature (having previously selected a certain mass in a certain volume, *i.e.* a certain concentration) the pressure will adjust itself to a certain value characteristic of the equilibrium state. In the case of liquid water in contact with water vapour in an enclosed vessel, if we arbitrarily choose a certain temperature then the other parameters will be fixed when the system is in equilibrium, *i.e.* the pressure is the pressure of saturated vapour at this temperature, and the concentration or density terms of the liquid and vapour phases have certain values. Such considerations as these, namely, the number of factors which define equilibrium and their interdependence, will be

taken up in dealing with the Phase Rule. For the present we shall proceed along somewhat different lines.

An equilibrium state is defined as, that state reached when some thermodynamic quantity (called a "thermodynamic potential") has reached its limiting value, *i.e.* either a maximum or minimum according to the particular potential employed. We have to find out what thermodynamical potential we must regard as justifiable to apply to the various cases which occur. Free energy is one of the thermodynamical potentials, and as we are familiar with it (Chap. I., Vol. II.), we can commence by saying that the free energy of any system tends to *decrease.* Notice particularly, however, that we do *not* say equilibrium in general is reached when the free energy of the system is a minimum. This latter statement as *a general* law would be quite untrue, as will be shown later.

We must, in fact, first postulate two things: (1) that the temperature is supposed to be maintained constant, and (2) that the reaction under consideration can proceed without a volume change. Now scarcely any reaction takes place without a volume change, but in condensed systems, as van 't Hoff called them, that is in systems either liquid or solid (homogeneous or heterogeneous) we can imagine the reaction to occur *practically* without a volume change.

The criterion of equilibrium being reached in such a reaction, i.e. *in one in which the temperature and volume are maintained constant, is simply that at the equilibrium point the Free Energy is a minimum, and therefore if we consider the system when equilibrium is reached and imagine the reaction to go to a small extent, namely, the transformation of* δn *molecules from one side of the equilibrium to the other, then the work done or free energy change is zero.* This is written algebraically $(\delta f)_{Tv} = 0$.[1]

We can likewise denote this by $(\delta A)_{Tv} = 0$, where A denotes external work.[2] Practically all the external isothermal reversible mechanical work processes with which we have to deal consist simply of the three-stage work process already discussed at some length. Although this process involves a vaporisation step, which is one entailing a large volume change, the final step of the process entails a condensation, and it is therefore possible to conceive of this three-stage process as being carried out *practically* without a volume change. Let us think of the system ice and water not in equilibrium at some temperature below 0° C., but under the pressure of their own vapours. There is a tendency of the water to solidify, this being a chemical reaction as much as any other reaction is. We can imagine 1 mole of the substance (water) trans-

[1] Those familiar with the principle of maxima and minima in the differential calculus will see that the above equation represents mathematically a maximum point on a continuous curve as well as a minimum. More strictly we should write for the equilibrium criterion $(\delta f)_{Tv} \geqq 0$; but the physical or chemical significance of the equality relation, *viz.* $(\delta f)_{Tv} = 0$, will cause no confusion.

[2] This is known as the chemical application of the Principle of Virtual Work. For an account of Virtual Work in Mechanics, for example, see A. W. Porter's book, *Intermediate Mechanics.*

ferred by the three-stage distillation process from the liquid water to the ice (at constant temperature), the work A amounting to $\int_{II}^{I} vdp$, which will be a positive work output (and therefore a real decrease in free energy) if the vapour pressure over the water (I) is greater than that over the ice (II). Experience has shown that below 0° the vapour pressure over the liquid (super-cooled and meta-stable water) is greater than that over ice, so there is a real decrease in f in the system when the liquid water becomes solid. Now the actual change in volume in this reaction is exceedingly small, it being simply the difference of the molecular volumes of ice and water respectively, for the total change in volume in any reaction is evidently the final volume reached *minus* the initial volume, no matter what volume changes may have occurred en route. We can thus imagine that the transformation of liquid water to ice *can* take place at constant temperature and volume. Ice and water are in equilibrium by definition when $(\delta f)_{Tv}$ or $(\delta A)_{Tv} = 0$. Suppose they are in equilibrium (experiment shows that one such equilibrium state will be reached when T is 273 + 0·007°, and the pressure is the vapour pressure of the substances). If we imagine a small quantity, δn moles, of water transferred, say, from ice to liquid water under these conditions, then according to definition we must set Work = zero. Now the work is evidently given by $\delta n \int_{II}^{I} vdp$, and in order that this may be zero it is evident that the pressure of the ice and of the water (I and II) must be *identical* so as to make $dp = 0$. This is an experimental fact, *viz.* ice and water are in equilibrium when the vapour pressures are identical, and this occurs at + 0·007° C. when water is under its own vapour pressure. Equilibrium is also reached at 0° C., when these pressures are modified by the presence of the atmosphere though again the vapour pressures of both (ice and water) are identical. [Note: The effect of an inert gas on the vapour pressure has already been dealt with at the end of Chap. I.]

Or take the reaction involved in the transformation of rhombic into monoclinic sulphur, or grey tin into white tin. By following exactly the same process of reasoning and carrying out an imaginary work process at constant temperature and volume, we find that the allotropic forms are in equilibrium when the vapour pressures are identical. Again the reaction between liquid water and sulphuric acid may also be reached at constant temperature, and practically constant volume; for any change in volume in the whole, is the difference of molecular volume of the water in the pure state, and its volume in sulphuric acid solution—a quantity which is not large. The principle that equilibrium is reached when $(\delta f)_{Tv} = 0$, or $(\delta A)_{Tv} = 0$ will apply, for here again the three-stage distillation process must be zero at the equilibrium point, which requires that the pressures over the water and strong sulphuric acid solution shall be equal. But this we know by experience can never be reached as long as *any liquid* water remains; for the vapour pressure over pure water is always greater than the vapour pressure over solutions

containing water (at the same temperature), and hence the criterion leads us to expect that equilibrium can only be reached when all the liquid water disappears and the vapour pressure falls to that over the sulphuric acid water solution. This is what actually happens.

Further, the criterion that equilibrium is reached when $(\delta A)_{T v} = 0$, applies to reactions in solutions. Take the simplest case of diffusion of a solute from a region of high concentration to one of low. Equilibrium is reached when the work entailed by a small virtual change in the system can be equated to zero. Suppose we have a solute at concentrations c_1 and c_2 and osmotic pressures P_1 and P_2 in the same vessel. By means of osmotic membranes (the whole vessel being supposed to be surrounded by solvent of infinite extent) we can imagine δn moles transferred from P_1 to P_2 the work being $\delta n \int_{P_2}^{P_1} v dP$, which will be zero when $P_1 = P_2$ or $c_1 = c_2$; that is equilibrium is reached when the concentration is the same throughout the vessel; this we know is an experimental fact.[1]

Or, again, take the case of pure benzene on the one hand and a saturated solution of benzene in water on the other, both systems being at the same temperature. A saturated solution of benzene is necessarily in equilibrium with pure liquid benzene itself because of the fact of saturation. The conclusion to be drawn from the thermodynamic criterion considered is, that under these conditions, $(\delta A)_{T v} = 0$, and therefore, if we imagine one mole of benzene transferred from the pure benzene to the saturated solution, the work must be zero. That is, there must be the same vapour pressure over the pure benzene as there is over its saturated solution in water, the vapour in each case being *benzene* vapour. In the case of a hydrated salt on the one hand and the saturated solution of the salt on the other, the conditions are more complex. We shall consider this point in Chap. X. in connection with the application of the Phase Rule to two component systems.

The criterion we have been considering breaks down, however, when the reaction cannot be conceived of as occurring with even approximately constant volume. Thus, take the reaction such as vaporisation or sublimation, *i.e.* change from a condensed to a gaseous system not followed by condensation. This can be carried out at constant temperature, but not at constant volume, though it can be done at constant pressure. We know from experience that equilibrium

[1] When we consider the transfer of a certain mass of a solvent to a solution in a thermodynamic manner, it is always necessary to think of the vapour pressure or the concentration or the osmotic pressure of the solution as remaining unchanged, *i.e.* we must not alter the final state itself as a result of the thermodynamic process. Thus, if we think of a *limited* quantity of a solution containing H_2SO_4 in water, it is necessary to transfer an infinitely small quantity of water, δn moles as in the above case. Instead of transferring δn moles, we might conceive of the transfer of one mole—a finite quantity—to a *practically infinite* quantity of the solution, no sensible change being brought about in the concentration of the solution as a result of the act of transfer itself. This idea of keeping the initial and final states unchanged whilst the process takes place is essential to all such thermodynamic processes.

is reached when the vapour has reached saturation pressure, but when we consider such a system in the equilibrium state, and suppose a quantity, δn moles, say, vaporised, the work is not zero; the work is the pressure into the change in volume. We must infer, therefore, since work is done by the system in passing from liquid to vapour, that the free energy, say, of 1 gram or 1 gram-mole of liquid is greater than the free energy of 1 gram or 1 gram-mole of saturated vapour at one and the same temperature, even though the liquid and vapour are in equilibrium. Obviously, if the free energy of the one phase is greater than the other, the free energy of the system is not a minimum. One must be careful, therefore, *not* to say that *in general* at a given temperature the equilibrium is reached when the free energy of the system is a minimum; for if this were so, then in the liquid-vapour system just considered one would expect the whole system to become vapour, since the vapour has less free energy; this is, however, contrary to experience. We must bring in the restriction that the process can be carried out at constant volume (or approximately so) as well as at constant temperature. In such a case the equilibrium *is* reached when the free energy is a minimum. It may be pointed out, however, that in the liquid-vapour equilibrium, although the free energies of a given mass of liquid and vapour respectively differ, there is a quantity called the "thermodynamical potential at constant temperature and pressure," which is denoted by the symbol Φ, and this has the same numerical value for 1 gram of saturated vapour as it has for the same mass of liquid at one and the same temperature. In reactions which occur with change of volume, but at constant temperature and pressure, equilibrium is reached when the Φ of the system is a minimum. To appreciate the significance of the thermodynamical quantity Φ we must, however, present the First and Second Laws in a more analytical way than we have done in the chapter in the "Elementary Treatment". For those who have followed the chapter on the "more advanced treatment" (Chap. II.) a short discussion of the Φ function is added to the present section. Before leaving the consideration of reactions which can be carried out at constant volume (approximately) and at constant temperature, it is essential to speak of those which are capable of losing free energy in the form of electrical energy, the reacting substances being set up in the form of a cell. The importance of this is due to the fact that where a cell is capable of being set up at all, the measurement of the electromotive force, which can be always carried out with great accuracy, gives us quantitative information of *exactly how far* the system is from the equilibrium point. We shall have occasion later on to make great use of this in the measurement of affinity.

Consider the reaction which takes place when a piece of metallic zinc is placed in a solution of copper sulphate. Copper is precipitated in the metallic form, and zinc sulphate solution is produced. The reaction is written in the form—

$$Zn + CuSO_4aq = Cu + ZnSO_4aq.$$

In terms of ions we can represent it by—

$$Zn + Cu^{++} = Zn^{++} + Cu.$$

If this reaction simply takes place in a test-tube, heat is evolved, but no work is done. If the tube be immersed in a thermostat, the reaction can be made to go at practically constant temperature and volume. To get work from this reaction, and especially to get the maximum work from it, it is necessary to make it proceed reversibly by means of a suitable thermodynamic arrangement. This arrangement is very nearly realised by the setting up of the system in the form of an electrolytic cell, *i.e.* the Daniell cell, having an electrode of copper immersed in copper sulphate solution, and an electrode of zinc in a zinc sulphate solution. Under these conditions, electrical energy (electromotive force × quantity of current) can be obtained from the cell, *i.e.* from the reaction. The cell must be made to work reversibly if there is to be production of maximum work. Suppose the cell possesses an e.m.f. of E volts (measured electrostatically, or, what is the same thing, with an extremely large resistance in the outer circuit), and is made to drive something which possesses a back e.m.f. of E − dE volts, then the cell is just able to do the work required of it and nothing more. Note that we must always reckon energy per certain quantity of substance (say, copper) transformed in the sense of the reaction studied. It is usual, especially in electrical measurements, to consider the gram equivalent as the unit of mass transferred. Now, the amount of electricity associated with 1 gram equivalent is 1 faraday, so that if the e.m.f. of the cell is E, and 1 gram equivalent is transformed, the electrical energy output is—

$$\text{E} \times 1 \text{ faraday} = \text{E} \times 1 = \text{E}.$$

That is, the numerical value in volts of the e.m.f. itself gives us the electrical energy (in volt-faradays) produced per gram equivalent, and from a measurement of the e.m.f. of the cell in the manner indicated, we can then say that the maximum work, electrical in form, which the reaction is capable of producing at the given temperature and practically without volume change, is E energy units per equivalent of one of the substances transformed. Notice that measuring the e.m.f. in this way gives us the same result as if we had set up some machine having an opposing e.m.f. of E − dE volts, and allowed the cell to drive this infinitely slowly. This is quite analogous to the idea of a piston moving and doing mechanical work with the pressure on the two sides only differing by dp. In fact, electromotive force can be regarded as "electrical pressure" (though one cannot give it the *dimensions* of pressure, namely, $\frac{\text{M}}{\text{LT}^2}$). Further, the reversibility of the Daniell cell is completed by the reaction being of such a kind that an external e.m.f. of magnitude E + dE applied in the opposite sense to that of the cell is capable of causing the chemical reaction also to reverse itself without the production of substances (such as O_2 and H_2) not previously present in the system. In brief, the electrodes must be reversible in the electrochemical sense (see later Nernst's *Osmotic Theory of Electromotive Force*), that is, the cell must not be polarisable; and the direct and reverse chemical processes should be capable of an infinite number of alternate

repetitions without any permanent change in the composition of the cell. Such a cell, working at constant temperature and producing electrical energy infinitely slowly, is the nearest practical approach to the ideal conception of a thermodynamic reversible isothermal process.

If, instead of working the cell so as to give maximum work, we go to the other extreme and short circuit the electrodes, thereby allowing the reaction to go quickly, the cell runs down, the e.m.f. finally being zero, *i.e.* the cell is no longer capable of doing any work. The equilibrium point of the reaction—

$$Zn + Cu^{++} \rightleftarrows Cu + Zn^{++}$$

is then reached. If now we analyse the solutions in the cell, we find that practically [1] all the copper is deposited, and the liquid is a solution of zinc sulphate, containing a certain amount of Zn^{++}. If we had simply allowed the reaction to occur in a test-tube (starting with the same amount of copper sulphate solution and adding metallic zinc), we would find on analysis that the amount of zinc in solution is the same in both cases. The fact that the e.m.f. becomes zero is experimental evidence that the equilibrium is reached when $(\delta A)_{TV} = 0$.

The consideration of the Daniell cell will have made clear the distinction to be drawn, as far as work production is concerned, between the spontaneous or irreversible mode of carrying out a reaction and the reversible mode (in the thermodynamical sense) of carrying out the same reaction, even though the end point reached is identical in both cases. In both cases there is the same decrease in the free energy of the system, but in the test-tube this has not been converted into work being simply dissipated as heat.

Applications of the Foregoing Principles to the Transformation of Allotropic Solids.

The systems we are about to consider are those consisting of *allotropic solids*, *i.e.* different crystalline modifications of the same chemical substance which possess the property of transformation the one into the other, the direction of the transformation depending on the temperature. Such systems are characterised by the existence of a *transition point* or *transition temperature* at which the different crystalline forms of the one substance are in equilibrium with one another. (The reason why such substances exhibit a transition temperature will be given when we come to apply the Phase Rule. For the present we are simply dealing with the phenomenon as an experimental fact.) At temperatures below the transition point one crystalline form is unstable, *i.e.* tends to pass entirely into the other. Above the transition point the second phase is now unstable and will pass entirely into the first. All these changes occurring at a given temperature involve practically no change in volume, and we can therefore apply the criterion that at equilibrium

[1] The infinitely small quantity of copper remaining in solution in this particular reaction is far below the limits of the most delicate analysis.

$(\delta A)_{TV} = 0$, or $\int_{II}^{I} vdp = 0$, where the integral stands for the familiar three-stage distillation work process. We shall apply this criterion to prove the following statements, each of which has been demonstrated by experiment:—

(1) At the transition temperature the vapour pressures of each modification is the same, and the solubility in a given solvent is the same.

(2) At any given temperature the stable modification has a smaller vapour pressure than the unstable, the temperature here considered is necessarily not the transition point.

(3) At any given temperature other than the transition temperature the stable modification has a smaller solubility than the unstable in a given solvent.

(4) The stable modification has a higher melting point than the unstable form.

(5) The ratio of the solubilities of the two forms (at a given temperature) is independent of the nature of the solvent.

1. *At the Transition Point the Vapour Pressures of both Modifications are Identical, as are also their Solubilities in a Given Solvent.*

At the transition point by definition the two modifications are in equilibrium. If now a mass δn be transferred isothermally and reversibly (by means of the three-stage distillation process) from modification I to modification II, the work must be zero, *i.e.* ($\delta A_{TV} = 0$, which in this case becomes $\delta n \int_{II}^{I} vdp = 0$). Since δn and v are positive terms, it follows that in order to make the work expression zero, dp must be zero; in other words, that the vapour pressures over I and II must be identical, which was to be shown. Further, we could imagine the same virtual work process carried out not by distillation but by means of osmotic work involving three stages. The two modifications are supposed to be in contact with a saturated solution of each in two vessels. The same solvent is of course employed and the whole system may be imagined as immersed in a bath of the solvent. By means of a piston permeable to solvent but impermeable to solute, the quantity δn moles of modification I is dissolved by drawing out the piston, the solution containing this quantity at osmotic pressure P_I being now expanded, *i.e.* diluted to osmotic pressure P_{II}, and then compressed into the saturated solution of modification II at osmotic pressure P_{II}. The total work is $\delta n \int_{P_{II}}^{P_I} vdP$, and this must be zero, which means that P_I must be identical with P_{II}. If the substance in solution obeys the gas laws, the identity of osmotic pressure means identity of concentration, and since solid was present in each case this means identity of solubility as was to be shown.

2. *At any other Temperature the Stable Modification has a Lower Vapour Pressure than the Unstable at the same Temperature.*

We commence by taking it as true that the meta-stable always tends to pass into the stable. This tendency only exists in virtue of the system being ready to do positive work. Let us imagine the transfer of δn moles from the unstable modification to the stable modification; p_0 refers to the vapour pressure of the unstable modification, and p_1 to that of the stable. The three-stage work done is, $\delta n \int_{p_1}^{p_0} v dp$. If the vapours obey the gas laws, we can write—

$$\delta A = \delta n RT \log \frac{p_0}{p_1}.$$

Now since the transfer has taken place from the unstable to the stable modification, this must mean that *positive* work δA is done by the system. Since δA is positive, $\log \frac{p_0}{p_1}$ must be positive. That is p_0 must be greater than p_1. But p_0 is the vapour pressure of the unstable phase. Hence the vapour pressure of the unstable modification is greater than that of the stable. (It will be observed that this would also hold even if the vapours do not obey the gas laws, for in order that $\int_{p_1}^{p_0} v dp$ may be positive the upper limit p_0 must be greater than the lower limit p_1.)

3. *The Unstable Modification has the Greater Solubility.*

One pursues exactly the same train of reasoning as in Case 2, using, however, osmotic pressure instead of vapour pressure. Again, the term $\delta n \int_{P_1}^{P_0} v dP$ must be positive in transferring δn moles *from* the saturated solution of the *unstable* modification (osmotic pressure P_0) *to* the saturated solution of the stable modification (osmotic pressure P_1). That is, P_0 must be greater than P_1, or the saturation concentration (*i.e.* solubility which is taken as proportional to osmotic pressure approximately) of the unstable modification is *greater* than the solubility of the stable modification at the given temperature. We can represent the behaviour of the vapour or saturated osmotic pressure of the two modifications α and β graphically thus (Fig. 15). At temperatures below the transition point the α modification has a lower vapour pressure or

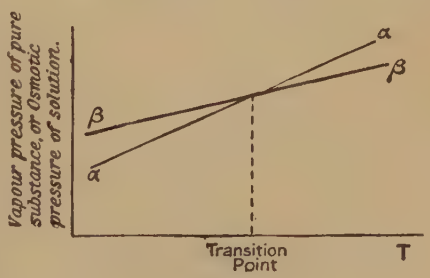


FIG. 15.

osmotic pressure, that is, the α is the stable modification on this side of the transition point. The vapour pressure and osmotic pressure curves are naturally continuous curves, and by producing them beyond the transition point we see that at temperatures higher than the transition temperature the β modification has now the lower vapour and osmotic pressures, that is, in this range the β is the stable modification. (The vapour pressure and temperature curves will in general not be straight lines as shown, but this is immaterial.)

4. *The Stable Modification has the Higher Melting Point.*

Let us denote the stable modification by α (Fig. 16), the unstable modification by β, the fused liquid produced on melting by γ. The line α, α denotes the vapour pressure over the α modification; the line β, β, the vapour pressure over the β modification; and the line γ, γ, the vapour pressure over the liquid. The transition point of α into β lies far to the left of the diagram; the lines α, α and β, β approach one another at lower temperatures. If we take any temperature T_1 it will be seen that the vapour pressure over the unstable solid (β) is greater than that over the stable solid (α). The position N denotes the melting point (melting temperature) of the stable modification; M the melting point of the unstable. Hence the stable phase must show the higher melting point. This conclusion rests essentially on the statement which we proved in Case 2, namely, that the vapour pressure of the stable modification at any given temperature is lower than that of the unstable form. The diagram also illustrates that *unstable* forms, *whether solid or liquid*, have a higher vapour pressure than the stable form at the same temperature. Thus let us take the dotted line Mγ. This is the vapour pressure of the super-cooled liquid, *i.e.* the liquid form should have changed entirely into the solid modification β at the temperature M, but it has not done so. Hence Mγ represents an unstable liquid phase, *i.e.* unstable with respect to the β modification and hence for a temperature such as T_1 the vapour pressure of the unstable super-cooled liquid is higher than that over the solid β modification into which the liquid should have been transformed at M. It happens that the solid β modification itself is unstable with respect to the α modification at the same temperature T_1 so that at T_1, if there is any super-cooled liquid in the system it must be very unstable indeed with respect to the

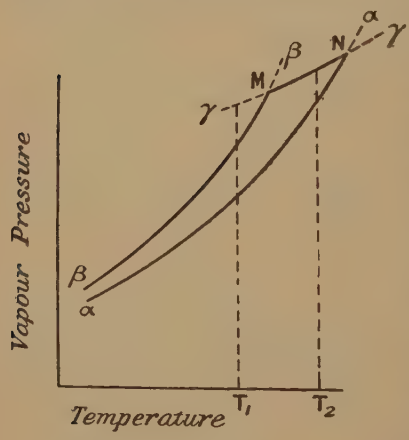


FIG. 16.

α solid modification. On the other hand, at temperatures above M the liquid form is stable compared to the solid β form, as is shown by the curve Mβ (the vapour pressure curve of the superheated solid β above its melting point) lying above the MN curve, which gives the vapour pressure of the liquid. The position of the curve NM shows, however, that the liquid in this temperature region is unstable with respect to the solid modification α, as can be seen by considering a temperature such as T_2, when the MN curve of the liquid lies above the curve for the solid α modification. At the melting point N the α solid and the liquid are in equilibrium. At temperatures higher than this the liquid is the stable form, the superheated solid α being unstable as is shown by the relative positions of the curves Nα (dotted) and Nγ. Note that in practice solids superheated above their melting points have never been realised.

As a matter of fact, in the system considered we are dealing with a special state of things reached when transformation is brought about *rapidly*. What happens in the case of enantiotropic substances, *i.e.* those which show a transition temperature below the melting point, is that on slowly heating up the change takes place, the system then consisting of a single stable modification (α) which possesses, of course, a single melting-point, *i.e.* N. By carrying out the heating process very rapidly, however, we can realise such a point as M, *i.e.* we can cause the unstable variety (β) to melt before it has had time to change over into the stable. These equilibrium relationships between phases will not be discussed further until we take up the Phase Law. It is sufficient for the present to have proved the statement that the stable modification has the higher melting point.

A further case of equilibrium between different crystalline forms of considerable interest may be mentioned, namely, that of grey tin and white tin, which are in equilibrium at a certain temperature and pressure (the transition point). The reaction goes practically without a volume change at a given temperature and equilibrium is reached when $(\delta A)_{TV} = 0$, which can be put in the form $\int_{II}^{I} v dp = 0$. We must therefore infer that the two forms are in equilibrium when their vapour pressures become identical. Further, this system is of interest because it can likewise be set up so as to yield electrical energy. Thus the cell—

White tin | Tin salt solution | Grey tin

will furnish an e.m.f. At the transition point this e.m.f. is zero, *i.e.* white and grey tin are in equilibrium. By means of a cycle we can show that this latter relation, *viz.* E = 0, must hold at the point at which the vapour pressures over the white and grey tin are identical, *i.e.* the transition point. Consider some temperature *other* than the transition point, and further consider 1 gram equivalent of white tin to be vaporised, the pressure changed from p_0 to p', where p' is the vapour pressure over grey tin at the same temperature, and then the vapour to be condensed into the grey tin. The work done up to this point is

$\int_{p'}^{p_0} v dp$. Assuming the white tin to be the unstable form, this work term is positive work done *by* the system. Now let the gram equivalent of grey tin be transferred electrically to the white tin by dissolving off the grey tin electrode and depositing on the white, *i.e.* current passes *through* the cell from grey tin to white. If the e.m.f. is E the work is E × F, where F is the faraday = 96540 coulombs, the amount of electricity carried by one gram equivalent of an ion. This work must have been done by some external agency *upon* the system itself, for the natural direction in which the system (the cell) tends to do electrical work is in the opposite sense, *i.e.* the cell itself tends to work in such a way as to dissolve the unstable white form and precipitate grey tin, so that eventually there will be nothing but grey tin present. Since E × F represents work done by the surroundings, then − E × F represents the work done by the system. The cycle is now complete, and since it is isothermal and reversible, the total work must be zero by the Second Law. That is—

$$\int_{p}^{p_0} v dp + (- \mathrm{E} \times \mathrm{F}) = 0,$$

or

$$\mathrm{E} \times \mathrm{F} = \int_{p'}^{p_0} v dp.$$

In general we can say that the electrical energy is just equal to the three-stage distillation work. Now at the transition point—

$$p_0 = p'. \quad \therefore \int_{p'}^{p_0} v dp = 0. \quad \therefore \mathrm{E} = 0.$$

We reach the same conclusion of course by following out the very similar type of reasoning involved in the principle of virtual work.

Suppose the grey tin and white tin are in equilibrium. Then in the transfer of δn moles from grey to white the work at constant temperature and volume is zero. Carrying the process out by the distillation method we see that at equilibrium $\delta n \int_{\text{white}}^{\text{grey}} v dp = 0$, or the vapour pressures over the modifications are identical. Also at the equilibrium point suppose a quantity δn moles transferred electrically through the solution from the grey to the white tin electrode. Suppose the e.m.f. is denoted by E and the electrochemical equivalent [1] of tin by α_{sn}, then the electrical work in volt-faradays is $\frac{\delta n}{\alpha_{sn}} \times \mathrm{EF}$. This must be zero. Since F and δn are positive terms and α_{sn} represents a positive quantity, it follows that E = 0, which was to be shown.

[1] The electrochemical equivalent of a substance is here defined as the mass in moles of the substance with which one faraday of electricity is associated when the substance is in the ionic form. The expression $\frac{\delta n}{\alpha_{sn}}$ denotes therefore the quantity of electricity associated with δn moles.

5. *The Ratio of the Solubilities of the Allotropic Forms at a given Temperature is Independent of the Nature of the Solvent.*

At the transition temperature, the solubility of the two forms in *any* given solvent is the same; that is, the ratio is unity. This conclusion is obviously involved in the considerations of Case I. We are now thinking, however, of a different set of conditions, *i.e.* a temperature which is *not* the transition temperature. Each allotropic form has its own solubility and the ratio is not unity. We have to show, on theoretical grounds, that although not unity, the ratio possesses a constant value independent of the nature of the solvent.

Consider forms I. and II. of a given substance. Let us suppose that the respective solubilities in a solvent A are C_{IA} and C_{IIA}. We shall further suppose that even the saturated solutions are sufficiently dilute to justify the applicability of the gas law. The *maximum* work obtainable on transferring δn moles from the solid in contact with the first solution to the solid in contact with the second is—

$$\delta n \int_{P_{IIA}}^{P_{IA}} v d\mathrm{P} = \delta n \mathrm{RT} \log \frac{P_{IA}}{P_{IIA}} = \delta n \mathrm{RT} \log \frac{C_{IA}}{C_{IIA}}.$$

The maximum work obtainable on transferring δn moles from the first solution to the second when the solvent is B, is—

$$\delta n \mathrm{RT} \log \frac{C_{IB}}{C_{IIB}}.$$

Now, the *same* solids are in equilibrium in both cases, not only with each other, but with respective saturated solutions, and we have really carried out the same process in the case of each solvent, *viz.* the transfer of δn moles of the material from solid I. to solid II. Further, the work done in each case is maximum work, and is therefore the same for both, for we start from a given point and end on another point, the same in both cases, and therefore the decrease in free energy must be the same. Hence, $C_{IA}/C_{IIA} = C_{IB}/C_{IIB}$ = a constant, which is the desired result. The same conclusion may be reached more easily by observing that the expression for the maximum work does not involve the solvent and is therefore independent of the nature of the solvent.

The above conclusion has been tested recently by Chattaway and Lambert (*Trans. Chem. Soc.*, **107**, 1773 (1915)) in the case of the two allotropic forms of phthalylphenylhydrazide, one of which is a deep yellow, the other a pale yellow solid. The two forms have widely

Solvent.	Solubility of Pale Yellow Modification.	Solubility of Deep Yellow Modification.	Ratio.
Benzene . . .	0·910	0·882	1·032
Alcohol . . .	0·913	0·883	1·034
Chloroform . . .	4·484	4·324	1·037
Ethyl acetate . .	4·654	4·489	1·037
Acetone . . .	10·060	9·693	1·038

differing solubilities in different solvents and hence the case is particularly suitable for our present purpose. The above table gives the solubilities of the two forms of the compound in five different solvents at 25° C. (the transition temperature itself being 55·25° C.).

It will be observed that the conclusion reached on the thermodynamic basis is borne out by experiment in a satisfactory manner.

Use of Entropy as a Criterion of Equilibrium.

The criterion of equilibrium which we have hitherto employed is that equilibrium is reached when the free energy is a minimum, or, in other words, if we imagine the change to occur to a further slight extent, *and the change must be one which can occur at a constant temperature and at constant volume*, then equilibrium exists if $(\delta f)_{Tv} > 0$. Although this is a suitable criterion to apply in certain cases it is unsuitable in others.

We can make the perfectly general statement that in any naturally occurring or spontaneous (and therefore irreversible) process which takes place in an isolated system the entropy of the system increases. The condition regarding the isolation of the system is fundamental. When we speak of an isolated system we mean one enclosed in a heat-tight case, heat being incapable of passing into or out of the enclosure. The direction of spontaneous change of any kind is necessarily towards the equilibrium point. Hence in the case of an isolated system we can say that the approach to the equilibrium state in a spontaneous process is accompanied by an increase in the entropy of the system. Hence *when equilibrium is reached the entropy is as great as possible, i.e.* a maximum, under the given conditions. This is the criterion of equilibrium in terms of entropy.

We have been speaking of a spontaneous and therefore of an irreversible process in the thermodynamic sense.[1] If, on the other hand, the process be carried out reversibly the entropy does not change at all in approaching the equilibrium position provided the system be isolated. Under no conditions, however, does the entropy diminish, provided the system be kept isolated. It is therefore immaterial whether we are dealing with, say, a chemical process accompanied by an absorption of heat (as ordinarily measured in the calorimeter) or with a process accompanied by an evolution of heat. If we think of the system in each case as being isolated we can say that the change towards equilibrium is accompanied by an increase in the entropy of the system, if the process be allowed to go spontaneously; if the process be caused to go reversibly, the entropy of the system does not alter. For all spontaneous changes in isolated systems we have therefore as a criterion of equilibrium that the entropy of the system has reached a maximum.

The above statements are simply the equivalent of what is expressed in the following equations:—

[1] Thermodynamic reversibility has of course nothing to do with reversibility in the chemical or Mass Action sense.

In the case of a reversible process the change in entropy is given by—

$$dS = dQ/T$$

where dQ is the heat taken in from the surroundings at the temperature T. In the case of an isolated system no heat can be taken in or given out. Hence in such a case $dQ = 0$, and therefore $dS = 0$, *i.e.* the entropy of the isolated system does not change during a thermodynamically reversible process. In the case of an irreversible process,

$$dS > dQ/T.$$

If the system be isolated in this case, dQ is again zero and therefore $dS > 0$, *i.e.* the entropy increases as a result of the physical or chemical change occurring spontaneously in the isolated system. To cover both reversible and irreversible cases we can write $dS \geqslant 0$.

The criterion of equilibrium, namely, that the entropy has reached a maximum value in the case of any process occurring spontaneously in an isolated system, will be employed later in Vol. III. when we are considering statistical equilibrium in systems composed of an enormous number of small units, *i.e.* molecules.

The Function Φ.

We saw in Chap. II. that for a reversible change in any system, we could write in general the increase in the total energy dU in the following way:—

$$dU = TdS - pdv - dw,$$

where TdS represents the increase in the heat content (the heat absorbed), pdv represents the mechanical external work done, and dw any other form of external work which may also have been done, *e.g.* output of electrical energy, capillary energy, radiant energy, gravitational work, etc. For practical purposes the term dw may be used to denote output of electrical energy. Since the process we are considering is reversible, all the work terms are maximum work terms. Now, from the above equation, since TdS must be equal to $d(TS) - SdT$, it follows that—

$$dU - d(TS) = -SdT - pdv - dw$$

or

$$d(U - TS) = -SdT - pdv - dw.$$

The quantity U represents the total energy of the system, the quantity TS is called by Helmholtz the bound or unavailable energy, so that the difference of the two, namely (U − TS), may be called the free energy (Helmholtz) and denoted by f. This is the strict definition of f. We can thus write the above equation—

$$df = -Sdt - pdv - dw.$$

Now if the process (reaction) which we are considering is one that goes, *i.e.* can be made to go, reversibly at constant temperature and volume, the terms SdT and pdv become zero, and the change of f is represented by—

$$(df)_{TV} = -dw.$$

(Note the negative sign denotes that positive work output *by* the system means decrease in free energy.) If we take as our standard of equilibrium, that equilibrium is reached when $dw = 0$; then $(df)_{Tv} = 0$. This is the same result we arrived at before, namely, in a reaction such as that in the Daniell cell which goes reversibly at constant temperature and practically constant volume, and reaches an equilibrium when the e.m.f. is zero. Consider such a system to have reached the equilibrium point, then we can say that if we imagine a change in either direction such change would be accompanied by an increase in free energy at constant temperature and volume, and would not therefore occur. The free energy of the system as a whole is a minimum, and the free energy of the reactants is equal to the free energy of the resultants at the equilibrium point.

Now returning to the equation—

$$d(U - TS) = - SdT - pdv - dw,$$

we can further transform this by writing—

$$pdv = d(pv) - vdp$$

into the relation—

$$d(U - TS + pv) = - SdT + vdp - dw.$$

This expression $(U - TS + pv)$ is denoted by Φ. If we consider a reaction made to go reversibly at constant temperature and pressure (such as vaporisation of water), we can see that any possible change in Φ can be expressed—

$$(d\Phi)_{TP} = - dw.$$

We take as our standard of equilibrium in a reaction which goes with a volume change, but can be made to go at constant temperature and pressure, that equilibrium is reached when $(d\Phi)_{TP} = 0$; that is again when dw is zero. In the case of water vaporising the term dw (electrical work) does not appear at all, and the equilibrium is reached at a given temperature, and a certain pressure, namely, the pressure of saturated vapour. Water and water vapour are in equilibrium when the Φ of 1 gram of water is equal to the Φ of 1 gram of vapour, and this occurs when the vapour is saturated. At the freezing point the Φ of 1 gram of ice = the Φ of 1 gram of liquid water, because the change can go at constant temperature and pressure. It can likewise go at constant temperature and volume, and hence $(df) = 0$ also. At the transition point the Φ of 1 gram of rhombic sulphur = the Φ of 1 gram of monoclinic sulphur, and similarly the Φ of 1 gram of grey tin = the Φ of 1 gram of white tin. The importance of Φ as defining equilibrium between phases (solid and solid (rhombic and monoclinic sulphur), solid and liquid (ice and water), liquid and vapour (water and water vapour)) will be apparent when we come to deduce the Phase Rule of Gibbs.

CHAPTER V.

Chemical equilibrium in homogeneous systems, from the thermodynamic standpoint—Gaseous systems—Deduction of the law of mass action—The van 't Hoff isotherm—Principle of "mobile equilibrium" (Le Chatelier and Braun)—Variation of the equilibrium constant with temperature—A special form of the equilibrium constant and its variation with pressure.

Van 't Hoff's "Equilibrium Box".

An "*equilibrium box*" is a vessel of unchangeable volume in which the various substances taking part in a given reaction are present in the equilibrium state. The walls of this vessel are suitably permeable to given substances and impermeable to others. It is only possible to apply the equilibrium box idea to a reaction taking place in a homogeneous system, *e.g.* gases or dilute solutions. Let us at present confine our consideration to a given reaction, *viz.* A + B = C + D. In the box the four substances A, B, C, D are present in equilibrium. Let us introduce isothermally and reversibly 1 mole of A and 1 mole of B into the box (through sides permeable only to each of these), at the equilibrium concentration or pressure; let us suppose that the chemical change takes place; then let us remove 1 mole of C and 1 mole of D (through sides permeable to these), also at the equilibrium concentration or pressure. What has happened is the transformation of A and B into C and D at the equilibrium concentration or pressure conditions, without the expenditure of mechanical work since the volume of the box is constant. Further, the system, *i.e.* the box and its contents, is at the end in exactly the same state as at the beginning, and this is true for all stages. No actual external work has been done in the chemical transformation under these conditions. If A and B are initially at an arbitrary pressure or concentration, work will be done either by or upon them in bringing them isothermally and reversibly to the concentration corresponding to equilibrium. When this stage has been reached they may be introduced into the equilibrium box where they might be imagined to react giving rise to C and D, which can be removed at the equilibrium concentration value, no work being done in doing this "in and out" operation.

Thermodynamic Deduction of the Mass Action Expression for Equilibrium in a Homogeneous Gaseous System.

We can do this by means of an isothermal reversible cycle. The proposition we make use of is that the sum of all the work terms for

a completed isothermal cycle add up to zero by the Second Law. Suppose the reaction is—

$$A + B \rightleftarrows C + D.$$

Suppose we have two reservoirs (Fig. 17) each containing four substances, A, B, C, D, *in equilibrium*, the absolute concentration terms in the one being C_A, C_B, C_C, C_D, and in the other γ_A, γ_B, γ_C, γ_D; each reservoir is an equilibrium box. The temperature is the same for both boxes.

First Step.—Take out 1 mole of A from reservoir I. isothermally and reversibly. In drawing out 1 mole of A at the partial pressure it has in I., say p_{A0}, the system does work $p_{A0}v_{A0}$, where v_{A0} is the volume of 1 mole of A at partial pressure p_{A0}.

First Sub-step.—Now alter v_{A0} to $v_{A'}$ reversibly, the pressure simultaneously altering to $p_{A'}$. Work done $= \int_{v_{A_0}}^{v_{A'}} p dv$. The mole is now at the partial pressure possessed by the same substance A in vessel II.

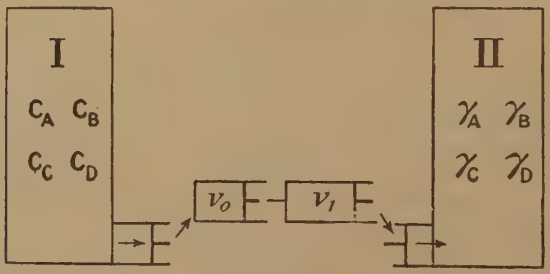


FIG. 17.

Second Sub-step with A.—Isothermally compress this mole into reservoir II., work done upon gas $= + p_{A'}v_{A'}$, and therefore work done by the gas is $- p_{A'}v_{A'}$. The first step plus these sub-steps we have already seen simply add up to the expression $\int_{p_{A'}}^{p_{A_0}} v_A dp$.

Second Step.—Along with the transfer of A we suppose a transfer of 1 mole of B from I. to II. to take place. Work per mole of B $= \int_{p_{B'}}^{p_{B_0}} v_B dp$.

Since the system is gaseous, let us assume the gas laws, and we can write—

$$p_{A_0} = RTC_A \text{ and } p_{A'} = RT\gamma_A$$

and hence—

$$\text{work term for A} = RT \log \frac{C_A}{\gamma_A}$$

$$\text{work term for B} = RT \log \frac{C_B}{\gamma_B}.$$

Third Step.—Now in this equilibrium box, *viz.* reservoir II., suppose the A and B we have added are changed into C and D, no external work being done.

Fourth Step.—Now transfer 1 mole of C and 1 mole of D from II. to I.

$$\text{Work} = \text{RT} \log \frac{\gamma_c}{C_c} + \text{RT} \log \frac{\gamma_D}{C_D}.$$

Finally let these molecules of C and D change into A and B in reservoir I., no work being done in either equilibrium box during the cycle as a whole. The cycle is now completed, the initial conditions being restored. Since this has been done isothermally and reversibly it follows from the Second Law of Thermodynamics that no work on the whole has been done. That is—

$$\text{RT} \log \frac{C_A}{\gamma_A} + \text{RT} \log \frac{C_B}{\gamma_B} + \text{RT} \log \frac{\gamma_C}{C_C} + \text{RT} \log \frac{\gamma_D}{C_D} = 0$$

or

$$\log C_A + \log C_B - \log C_C - \log C_D = \log \gamma_A + \log \gamma_B - \log \gamma_c - \log \gamma_D$$

or

$$\frac{C_A \times C_B}{C_c \times C_D} = \frac{\gamma_A \times \gamma_B}{\gamma_c \times \gamma_D} = \text{constant}.$$

The term "constant" is justified, for no numerical relation whatsoever was assumed to exist between C's and γ's beyond the fact that they corresponded in each reservoir to equilibrium at the same temperature. Hence we obtain the Guldberg Waage expression, or the Law of Mass Action for a system obeying the gas laws.

Note to Preceding Proof.

In working with an equilibrium box, in order that equilibrium shall always prevail, we must not alter the concentration of any one of the components. That is, as we introduce the reactants (say into vessel II.), we must simultaneously remove an equivalent quantity of resultants (which might be regarded as actually the transformed reactants which we are putting in). Similarly, in the case of vessel I. the addition and subtraction must be simultaneous. The cycle, though described as a series of consecutive effects, must really be imagined as taking place "everywhere at once," that is, disregarding the time factor in order that each equilibrium box may be at every moment a system possessing equilibrium concentration.

Another point requires mention. In the case chosen the reaction involved no change in the number of molecules, *i.e.* no increase in volume at constant pressure or increase in pressure at constant volume. It might seem, therefore, that the absence of work in the transformation from reactants to resultants (or *vice versa*) in the equilibrium boxes really depended on this property of the system. This is not the case, however. The conception of an equilibrium box and the principle of virtual work are quite as applicable to reactions which involve a change in the number of molecules. Thus take the case of the combination of 2 volumes of hydrogen with 1 volume of oxygen to form 2 volumes of water vapour. In the process going in this direction there is a decrease of 1 volume, but under the equilibrium box conditions and arrangement this loss of 1 volume in the box is exactly balanced by the fact that we *put in* 3 volumes and only *took out* 2. The contents of the box remain as they were, the volume of the box remaining constant. Of course in all cases there will be a positive or negative heat passing out from the box into the constant temperature reservoir with which it is in contact; such heat

being the equivalent of the total energy liberated or absorbed in the reaction, but no work comes out or goes in.[1]

The Law of Mass Action, as applied to homogeneous gaseous systems, has already been illustrated in Vol. I. by several concrete examples. It is unnecessary, therefore, to repeat or extend these in the present discussion of the law, as sufficient instances of its experimental verification have already been given.

As already pointed out in dealing with the Law of Mass Action from the kinetic standpoint, the principle holds good in the first instance for homogeneous gaseous systems. It can likewise be extended to the case of heterogeneous equilibrium, in which a gas or gases are essential to the reaction, *e.g.* the dissociation of calcium carbonate, or ammonium chloride. Every solid or liquid possesses a vapour pressure, however small, and hence in the vapour space above the solid calcium carbonate and lime we have some gaseous $CaCO_3$ molecules, gaseous CaO molecules, and a large quantity of gaseous CO_2 molecules. This space containing vapour can be treated as a homogeneous system in which a gaseous reaction can take place, and the equilibrium is determined by—

$$K = \frac{C_{CO_2}^{gas} \times C_{CaO}^{gas}}{C_{CaCO_3}^{gas}}.$$

This simplification which can be introduced here, however, is that the concentration terms for gaseous carbonate and lime are themselves constant (at constant temperature), since the solids are present and the corresponding vapours are therefore saturated. The equilibrium in such a case is thus defined by the CO_2 pressure alone, since this is not "saturated," *i.e.* no solid or liquid CO_2 is present. That is—

$$K = K'C_{CO_2}$$

or C_{CO_2} = constant at constant temperature.

The Van 't Hoff Isotherm.

This is an expression which gives the maximum external work which can be obtained from a given chemical process occurring in a gaseous system at constant temperature, the work being expressed in terms of the equilibrium constant. Later we shall see the significance of this "Isotherm" as a measure of the affinity of a reaction. For the present the expression will be deduced by the aid of thermodynamics (and the equilibrium box), as we require the isotherm in the subsequent consideration of the variation of the equilibrium constant K with temperature.

Deduction of the Van 't Hoff Isotherm.

Let us suppose that we are dealing with the reaction—

$$2H_2 + O_2 = 2H_2O$$

taking place in the gaseous state. The arbitrarily chosen concentration values of the hydrogen and oxygen are C'_{H_2} and C'_{O_2}, and we want to find what will be the maximum work output involved in making 2 moles of hydrogen and 1 mole of oxygen react thermodynamically, *i.e.* re-

[1] From the purely thermodynamical standpoint it is interesting to note that the change from reactants to resultants, even as it occurs in the equilibrium box, must be an irreversible process because it occurs naturally or spontaneously; but, regarded as a link in the chain of operations, the reverse change occurs in the box where the taking in and putting out operations are exchanged. Chemical reversibility is not the same thing as thermodynamical reversibility. There is really a difficulty here, however.

versibly, so as to end up finally with a system consisting of water vapour at an arbitrary concentration C'_{H_2O}. We imagine that there are three practically infinitely large vessels (Fig. 18) containing respectively H_2, O_2, and H_2O gases at the arbitrary concentration, C'_{H_2}, C'_{O_2}, C'_{H_2O}. The temperature is T throughout. The size of these three vessels is so great that on withdrawal or addition of 1 mole or even 2 moles of the constituent, this can be done without altering the concentration in the vessel, *i.e.* the mole of gas can be drawn off at constant pressure. Besides these three large vessels, we likewise suppose that we have at our disposal an equilibrium box containing H_2, O_2, and H_2O gases at the equilibrium concentrations $C_{\epsilon H_2}$, $C_{\epsilon O_2}$, $C_{\epsilon H_2O}$, corresponding also to the

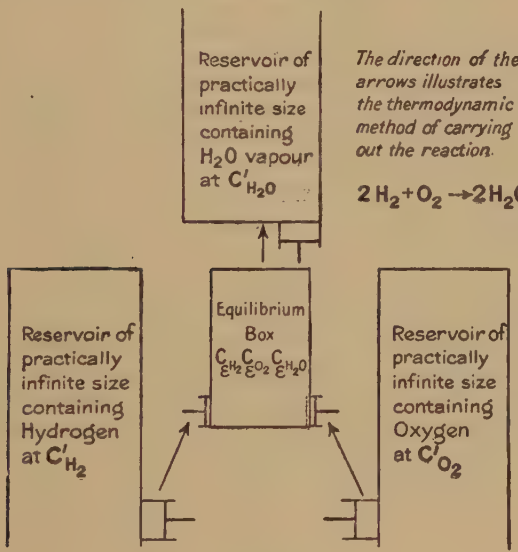

Reservoir of practically infinite size containing H_2O vapour at C'_{H_2O}
The direction of the arrows illustrates the thermodynamic method of carrying out the reaction.
$2H_2+O_2 \rightarrow 2H_2O$
Reservoir of practically infinite size containing Hydrogen at C'_{H_2}
Equilibrium Box $C_{\epsilon H_2} C_{\epsilon O_2} C_{\epsilon H_2O}$
Reservoir of practically infinite size containing Oxygen at C'_{O_2}

FIG. 18.

temperature T. One face of the equilibrium box possesses the property of being permeable to hydrogen and impermeable to oxygen or water. A second face is only permeable to oxygen, a third face permeable to water vapour only. Now we suppose the following thermodynamic process carried out:—

I. By means of a cylinder and piston one can take 2 moles of hydrogen from the stock at concentration C'_{H_2} to the equilibrium box (where hydrogen is at concentration $C_{\epsilon H_2}$) reversibly and isothermally, thereby accomplishing a three-stage process in which

$$A_{\text{per 2 moles of } H_2} = 2\int_{\text{final pressure in equilibrium box}}^{\text{initial pressure in infinitely large vessel}} vdp \text{ (where } v = \text{molecular volume)}$$

The gas is supposed to obey the gas law, so that we can evidently write

$$A_{\text{per 2 moles of } H_2} = 2RT \log \frac{C'_{H_2}}{C_{\epsilon H_2}}$$

the number "2" entering in because 2 gram-molecules have been transferred. C'_{H_2} is the initial concentration, $C_{\epsilon H_2}$ the final concentration reached in this process.

II. Simultaneously with operation I. we suppose 1 gram-mole of oxygen is taken from the stock vessel at C'_{O_2} to the equilibrium box at $C_{\epsilon O_2}$. The work done is given by—

$$A_{\text{per 1 mole of } O_2} = RT \log \frac{C'_{O_2}}{C_{\epsilon O_2}}.$$

The hydrogen and oxygen now in the equilibrium box react without doing external work, water vapour being removed at the same time.

III. Two moles of water vapour are removed from the equilibrium box at concentration $C_{\epsilon H_2O}$, and brought to the vessel at arbitrary concentration C'_{H_2O}. The initial concentration in this case is $C_{\epsilon H_2O}$, the final concentration being C'_{H_2O}. Hence the work is given by—

$$A_{\text{per 2 moles of } H_2O \text{ gas}} = 2RT \log \frac{C_{\epsilon H_2O}}{C'_{H_2O}}.$$

The total process which has been carried out isothermally and reversibly is simply the chemical combination of 2 moles of H_2 and 1 mole of O_2 at a given arbitrary concentration to produce H_2O vapour also at arbitrary concentration. If the total maximum work or decrease in free energy is A, then—

$$A = A_{\substack{\text{per 2 moles of} \\ \text{hydrogen}}} + A_{\substack{\text{per mole of} \\ \text{oxygen}}} + A_{\substack{\text{per 2 moles of water} \\ \text{vapour.}}}$$

that is—

$$A = 2RT \log \frac{C'_{H_2}}{C_{\epsilon H_2}} + RT \log \frac{C'_{O_2}}{C_{\epsilon O_2}} + 2RT \log \frac{C_{\epsilon H_2O}}{C'_{H_2O}}.$$

But the equilibrium constant K of the H_2O, O_2, H_2 reaction ($2H_2 + O_2 \rightarrow 2H_2O$), at temperature T, is—

$$K = \frac{C^2_{\epsilon H_2O}}{C_{\epsilon O_2} \times C^2_{\epsilon H_2}}$$

or $$\log K = \log C^2_{\epsilon H_2O} - \log C_{\epsilon O_2} - \log C^2_{\epsilon H_2}.$$

Hence the above expression for A may be written—

$$A = RT \log K - RT \log \frac{(C'_{H_2O})^2}{(C'_{H_2})^2 \times C'_{O_2}}.$$

It will be observed that the magnitude of A depends on how *far* the arbitrarily chosen concentration of the system is from the equilibrium concentration state. If the arbitrarily chosen state happens to correspond to the equilibrium state naturally no work will be done in reaching the equilibrium state. This the above formula expresses. It will also be observed that the above formula is deduced on the assumption that the system obeys the gas laws. Numerical illustration of this formula will be given when we come to study the affinity of a reaction. The most general mode of expressing the isotherm when several substances react, *e.g.*—

$$\nu_1 A_1 + \nu_2 A_2 + \text{etc.} = \nu'_1 A'_1 + \nu'_2 A'_2 + \text{etc.}$$

is simply to write the arbitrary concentration term in an abbreviated form, viz. $RT\Sigma\nu \log C$, where C stands for all the arbitrary concentration terms (the reactants in the denominator, the resultants in the numerator in the log term), and $\Sigma\nu$ simply stands for $\nu'_1 + \nu'_2 + \text{etc.} - \nu_1 - \nu_2 - \text{etc.}$, so that the general form of the isotherm is—

$$A = RT \log K - RT\Sigma\nu \log C.$$

The Principle of Le Chatelier and Braun, or "The Principle of Mobile Equilibrium".

This generalisation was first given by Le Chatelier in 1884, and later independently by Braun in 1887-88. No "proof" in the ordinary sense can be given of it; it is a generalisation based on experience. It has been applied in all branches of Physics and Chemistry, and has shown itself to be a valid and perfectly general law of nature. Since it involves no assumptions regarding molecular structure of systems, it is to be regarded as a thermodynamical law. As a matter of fact, it is comprehended in the Second Law of Thermodynamics. This connection is discussed very fully in Chwolson's *Textbook of Physics* (vol. iii. p. 474, *seq.*), to which the reader is referred for further information on this point.

The principle may be stated as follows:—

WHEN A FACTOR DETERMINING THE EQUILIBRIUM OF THE SYSTEM IS ALTERED, THE SYSTEM TENDS TO CHANGE IN SUCH A WAY AS TO OPPOSE AND PARTIALLY ANNUL THE ALTERATION IN THE FACTOR. THE SAME IDEA IS CONVEYED BY SAYING THAT EVERY SYSTEM IN EQUILIBRIUM IS CONSERVATIVE, OR TENDS TO REMAIN UNCHANGED. THAT IS, CONSIDERING A PHYSICAL OR CHEMICAL SYSTEM IN EQUILIBRIUM, THE EQUILIBRIUM BEING FIXED BY THE NATURE OF THE SYSTEM AND CONDITIONS SUCH AS TEMPERATURE AND PRESSURE, THE PRINCIPLE STATES THAT IF WE ALTER ONE OF THESE CONDITIONS OR PARAMETERS, SAY THE TEMPERATURE, THE SYSTEM WILL CHANGE IN SUCH A DIRECTION AS TO TEND TO ANNUL THIS CHANGE IN TEMPERATURE. The principle will be made clearer by a few examples.

Consider the case of a gas occupying a certain volume at a given pressure and temperature. Suppose the pressure is increased. The

volume is thereby decreased, and according to the principle the system ought to oppose this volume decrease. It does so in rising in temperature, for a rise in temperature tends to make the volume increase. We are familiar with the fact that by compressing a gas its temperature rises. This behaviour is in agreement with the principle. Take as another case a gaseous system such as iodine vapour partially decomposed and in equilibrium with its dissociation products at a given temperature and pressure. Now suppose the temperature of the system is raised. According to the principle the system will change so as to tend to annul this rise in temperature. What actually happens is that the dissociation of iodine molecules *increases*, and separate experiments show that a gaseous dissociation is accompanied by an absorption of heat. In a process involving heat absorption the temperature would naturally fall, and this fall of course opposes the rise in temperature impressed upon the system by the external agency in the first instance. The fact that gaseous dissociation *increases* with *rise* in temperature is thus directly due to the fact that the process of dissociation involves heat absorption. In cases of dissociation involving an evolution of heat, the principle leads us to expect that an increase of temperature will cause a decrease in the dissociation, *i.e.* a recombination of the dissociation products, since in this process heat is absorbed.

What has been said in connection with dissociation holds for all kinds of chemical reactions either homogeneous or heterogeneous. An endothermic reaction will be favoured by a rise in temperature, an exothermic reaction by a lowering of temperature. The effect produced, say, by increasing or decreasing the pressure on a gaseous system in equilibrium can also be predicted by the principle, provided we know whether the reaction considered involves a volume increase or decrease. This statement must not be taken as meaning that the equilibrium *constant* alters with the pressure. The equilibrium constant remains unchanged; otherwise no meaning could be attached to it as a constant in this case, for in gaseous systems our only means of obtaining isothermal variation in concentrations is by altering the pressure. In the case of the hydriodic acid dissociation which involves no change in volume the effect of pressure ought to be nil according to the principle, and this is in agreement with experiment as we have already seen in Vol. I. In the case of the dissociation process of $I_2 \rightarrow 2I$, the volume increases. Now if we increase the pressure the system will change in the chemical sense so as to annul this increase in pressure. It can do so by the dissociation *diminishing*, as thereby there are fewer molecules present, and the pressure of the system itself tends to be less than in the first instance. Notice that we are only employing the term "tends to be less". Actually the pressure of the system in the final state is greater than in the initial state, but it is not so great as it would have been if the extent of the dissociation had remained unchanged. The behaviour in this case is to be distinguished from that of a single gas in which no chemical reaction was possible, and in which we consider changes in pressure, temperature, and volume simultaneously. Of course in the

dissociation case also the temperature will tend to rise on compression if this be rapid, but after allowing sufficient time to elapse so that the temperature is the same as at the start, the dissociation will be found to have permanently diminished as already described. Instead of confining our illustrations to gases, let us consider a heterogeneous reaction involving solid and liquid phases, *e.g.* the process of solution of a solid in a solvent. Suppose we have a saturated solution of a substance, and some of the undissolved solid in contact with it at a given temperature. Now suppose the *temperature* is raised. Will the substance still further dissolve or will there be a precipitation of the substance already in solution? This depends entirely on whether the process of solution of the solid involves a heat evolution or absorption. If the solid dissolves with *absorption* of heat, the raising of the temperature will cause some more of the solid to dissolve since this tends to annul the temperature rise. For such a substance the solubility increases with the temperature. If the solid dissolves with *evolution* of heat, a rise in temperature will cause some of the solid to be precipitated from the solution, which at this higher temperature is now super-saturated, for by this process (the reverse of solution) heat is absorbed, and therefore the temperature rise is partly annulled, at least temporarily. Again consider the same system and suppose the pressure upon it increased at constant temperature. The system will change in the following way. Further solution of the solid will take place if the process of solution is accompanied by a contraction in volume of the system as a whole, as the contraction *tends* to annul the increase in pressure applied by a gas, say the atmosphere. On the other hand, some of the dissolved solid will be precipitated from solution if this process involves a volume decrease (a contraction).

The Variation of the Equilibrium Constant with Temperature. The van't Hoff Isochore.

The expression we are about to deduce is—

$$\frac{\partial \log K}{\partial T} = -\frac{U}{RT^2}$$

where K is the Mass Law equilibrium constant, U the decrease in total energy involved in the transfer of the necessary number of moles of reactants (required by the stoichiometric or ordinary chemical equation) into resultants, T the absolute temperature, R the gas constant per mole. This expression is known as the *van't Hoff Isochore*, and is simply the Le Chatelier-Braun principle applied quantitatively (by making use of the First and Second Laws of Thermodynamics) to the case of the effect of temperature on the equilibrium constant K of a given reaction. Suppose for simplicity's sake, we consider a gaseous system in which the reaction is—

$$\nu_1 A_1 + \nu_2 A_2 + \text{etc.} = \nu'_1 A'_1 + \nu'_2 A'_2 + \text{etc.}$$

The equilibrium constant K is—

$$K = \frac{[A'_1]^{\nu'_1} \times [A'_2]^{\nu'_2} \times \ldots}{[A_1]^{\nu_1} \times [A_2]^{\nu_2} \times \ldots}$$

Suppose we have a number of vessels each containing the substances A_1, A_2, A'_1, A'_2, at arbitrarily chosen concentration values. Then the work done in bringing the correct stoichiometric quantities (as required by the chemical equation), *i.e.* ν_1 moles of A_1, ν_2 moles of A_2, etc., into the "equilibrium box" and transforming them into resultants, and these being brought to the arbitrarily chosen concentration values, is given by A, where—

$$A = RT \log K - RT\Sigma\nu \log C \text{ (van 't Hoff's Isotherm).}$$

To find how this varies with temperature (at constant volume) it is only necessary to differentiate with respect to T, thus—

$$\left(\frac{dA}{dT}\right)_v = R \log K + T\frac{d}{dT}(R \log K) - R\Sigma\nu \log C - T\frac{d}{dT}(R\Sigma\nu \log C).$$

Now the arbitrarily chosen concentration values of the reactants and resultants, which are denoted by the terms $\Sigma\nu \log C$ are not a function of temperature or any other condition, being simply a matter of choice. That is, the expression—

$$\frac{d}{dT}(R\Sigma\nu \log C) = 0.$$

Further, dividing the isotherm by T, one obtains—

$$\frac{A}{T} = R \log K - R\Sigma\nu \log C.$$

Hence

$$\left(\frac{dA}{dT}\right)_v = \frac{A}{T} + RT\frac{d}{dT} \log K,$$

or

$$T\left(\frac{dA}{dT}\right)_v = A + RT^2\frac{d}{dT} \log K \quad . \quad . \quad . \quad (1)$$

Now the Gibbs-Helmholtz equation states that for any reversible reaction—

$$A - U = T\left(\frac{dA}{dT}\right)_v \quad . \quad . \quad . \quad . \quad (2)$$

by combining equations (1) and (2), we obtain—

$$\frac{\partial \log K}{\partial T} = -\frac{U}{RT^2}.$$

Since + U can be written $- Q_v$ where $- Q_v$ stands for heat evolved by the reaction at constant volume[1] we can write—

$$\frac{\partial \log K}{\partial T} = \frac{+ Q_v}{RT^2}$$

where $+ Q_v$ stands for heat absorbed.

[1] Even for reactions which do involve a volume change, the heat equivalent of the work done in expansion or contraction can be calculated and added to or subtracted from the value Q to give Q_v.

This equation, which is one of fundamental importance, holds not only for homogeneous gaseous reactions, but likewise for heterogeneous reactions as well as for solutions, as we shall see—in fact in all cases where a real significance can be attached to "K". Now suppose that in a certain case rise of temperature favours the production of resultants, *e.g.* dissociation. Since K is the ratio of resultants to reactants (raised to certain powers, ν'_1, ν'_2, ν_1, ν_2, etc.), an increase in the equilibrium concentration of *resultants* due to temperature means that K must numerically increase with temperature, *i.e.* $\frac{\partial \log K}{\partial T}$ must be a positive quantity. Hence $-\frac{U}{RT^2}$ must be a positive quantity, that is $-U$ must be positive. Now U denotes *decrease* in total energy, so $-U$ denotes increase in total energy, that is heat absorbed at constant volume. Hence in the case considered the reaction (dissociation) must be accompanied by heat absorption, that is the van 't Hoff Isochore is simply the quantitative form of the Le Chatelier-Braun principle of mobile equilibrium applied to the particular case of a chemical equilibrium.

Integration of the van 't Hoff Isochore.

The expression—

$$\frac{\partial \log K}{\partial T} = \frac{-U}{RT^2} = \frac{+Q_v}{RT^2}$$

is not of much use as it stands unless we can integrate it. As a first approximation which holds in a very large number of cases we can regard Q_v (the heat absorbed by the reaction) as practically independent of temperature provided we are not dealing with too wide a temperature range. Taking two temperatures, T_1 and T_2 ($T_2 > T_1$), not very far apart, and supposing that the heat at constant volume is Q_v at both temperatures, then the corresponding equilibrium constants K_1 and K_2 are connected with one another by the relation—

$$\log K_2 - \log K_1 = \frac{-U}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{Q_v}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right).$$

This may be illustrated by the following data, obtained in connection with the dissociation of nitrogen peroxide:—

$$N_2O_4 \rightleftarrows 2NO_2$$

(cf. Knox, *Physico-Chemical Calculations*, Problem 166). At a temperature 27° C. and 1 atmosphere pressure the equilibrium constant $K = \frac{C^2_{NO_2}}{C_{N_2O_4}}$ is 0·0017. At 111° C. the constant is 0·204. What is the heat of the dissociation per mole at constant volume?

We assume that over the range investigated $-U$ or Q_v remains constant. The expression just obtained then gives us—

$$Q_v = R \log \frac{K_2}{K_1}\left(\frac{T_1 T_2}{T_2 - T_1}\right)$$

$$R = 2 \text{ calories per mole approx.}$$
$$T_1 = 27^\circ \text{ C.} = 300^\circ \text{ absolute}$$
$$T_2 = 111^\circ \text{ C.} = 384^\circ \quad ,,$$
$$\therefore \underset{\text{(Heat absorbed)}}{Q_v} = 2 \times \log_e \frac{0{\cdot}204}{0{\cdot}0017} \times \frac{300 \times 384}{84}$$
$$= 13{,}110 \text{ calories.}$$

Another illustration (see Knox's *Physico-Chemical Calculations*, Problem 176).

The molecular heat of combustion of hydrogen is $Q_1 = -58{,}000$ cals., the minus sign denoting heat evolved; and that of carbon monoxide is $Q_2 = -68{,}000$ cals. What is the composition at equilibrium of the water gas formed from equal volumes of water vapour and carbon monoxide (1) at a temperature $T_1 = 800^\circ$ abs., and (2) at a temperature $T_2 = 1200^\circ$ abs.?

The reaction $H_2O + CO = H_2 + CO_2$ is made up of two subsidiary reactions—

$$(1)\ H_2O = H_2 + \tfrac{1}{2}O_2$$
and
$$(2)\ \tfrac{1}{2}O_2 + CO = CO_2.$$

The heat of reaction (1) is $Q_1 = +58{,}000$ cals., and of reaction (2) $Q_2 = -68{,}000$ cals. The heat effect of the total reaction

$$H_2O + CO \rightarrow H_2 + CO_2 \text{ is therefore—}$$

$Q = -Q_1 + Q_2 = -10{,}000$ cals., *i.e.* heat is *evolved*. The reaction is one which goes at constant volume. Hence Q is identical with Q_v. The equilibrium constant K alters with the temperature according to the relation—

$$\frac{\partial \log K}{\partial T} = \frac{Q_v}{RT^2}$$

where Q (*i.e.* $+Q_v$) denotes heat absorbed, and K as usual is defined as—

$$\frac{C_{eH_2} \times C_{eCO_2}}{C_{eH_2O} \times C_{eCO}}.$$

Let K refer to the temperature T and K_1 to T_1. Integrating the van 't Hoff expression we obtain—

$$\log_e \frac{K_1}{K} = \frac{Q_v}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right) \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

Similarly integrating between the temperatures T and T_2 we obtain:—

$$\log_e \frac{K_2}{K} = \frac{Q_v}{R}\left(\frac{1}{T} - \frac{1}{T_2}\right) \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

The value of K at $T = 1000$ abs. is found experimentally to be 3·26. The problem is first of all to calculate K_1 at the temperature $T_1 = 800$ abs. From equation 3 we have—

$$\log_{10} K_1 = \log_{10} K + \frac{Q_v \times 0{\cdot}4343(T_1 - T)}{RTT_1}.$$

In the reaction considered, the heat absorbed, Q_v, is a negative quantity (- 10,000 cals.), because the heat is really evolved. Substituting this value in the above expression we obtain—

$$\log_{10} K_1 = \log_{10} K - \frac{10{,}000 \times 0{\cdot}4343(800 - 1000)}{1{\cdot}985 \times 1000 \times 800}$$

$$= 0{\cdot}513 + 0{\cdot}552 = 1{\cdot}065$$

therefore $K_1 = 11{\cdot}6$.

On lowering the temperature, K has *increased* to K_1. That is, at the lower temperature, the concentration of the resultants is increased owing to the fact that their formation is accompanied by an evolution of heat which tends to maintain the system at the original temperature 1000 abs. The equilibrium constant K_2 refers to the temperature $T_2 = 1200$ abs. From equation four we have—

$$\log_{10} K_2 = \log_{10} K + \frac{-10{,}000 \times 0{\cdot}4343 \times (T_2 - T)}{1{\cdot}985 \times 1000 \times 1200}$$

$$= 0{\cdot}513 - 0{\cdot}364 = 0{\cdot}149$$

therefore $K_2 = 1{\cdot}41$.

If x_1 is the fraction of the water vapour transformed at T_1 according to the equation $H_2O + CO = H_2 + CO_2$, and x_2 the corresponding fraction at T_2, then, as in problem 175, we obtain—

$$\frac{x_1}{1 - x_1} = \sqrt{K_1} = \sqrt{11{\cdot}6} = 3{\cdot}40$$

$$x_1 = 0{\cdot}773;$$

and

$$\frac{x_2}{1 - x_2} = \sqrt{K_2} = \sqrt{1{\cdot}41} = 1{\cdot}19$$

$$x_2 = 0{\cdot}542.$$

The composition of the water gas mixture is, therefore, at $T_1 = 800°$ abs.—

$$38{\cdot}7\ \%\ CO_2;\ 38{\cdot}7\ \%\ H_2;\ 11{\cdot}3\ \%\ H_2O;\ 11{\cdot}3\ \%\ CO;$$

and at $T_2 = 1200°$ abs.—

$$27{\cdot}1\ \%\ CO_2;\ 27{\cdot}1\ \%\ H_2;\ 22{\cdot}9\ \%\ H_2O;\ 22{\cdot}9\ \%\ CO.$$

The assumption that Q_v or U is independent of temperature cannot be regarded, however, as anything more than an approximation. Experience has shown that U may be represented as a function of the temperature involving a series of ascending powers of T. Thus we can write for the total energy change of a gaseous reaction at any temperature the relation—

$$U = U'_0 + \alpha' T + \beta' T^2 + \text{etc.}$$

where U'_0 denotes the heat of the reaction in the neighbourhood of absolute zero. (Actually at the absolute zero the gaseous state can have no physical existence.) Employing the above expression for U, we can integrate accurately the van 't Hoff Isochore—

$$\frac{\partial \log K}{\partial T} = \frac{-U}{RT^2}$$

obtaining the expression—

$$\log K = \frac{U'_0}{RT} - \frac{\alpha'}{R}\log T - \frac{\beta'}{R}T - \frac{\gamma'}{2R}T^2 - \ldots + I$$

when I is the thermodynamically indeterminate integration constant. Later on, in discussing Nernst's Thermodynamic Theorem, Chap. XIII., we shall see how this constant can actually be evaluated. If we can simply consider integration between any *two* temperatures T_1 and T_2 to which the constants K_1 and K_2 respectively correspond, the integration constant of course vanishes, and we get—

$$\log K_2 - \log K_1 = \frac{U'_0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) - \frac{\alpha'}{R}\log\frac{T_2}{T_1} - \frac{\beta'}{R}(T_2 - T_1) - \ldots$$

The significance of the coefficients α', β', γ' will be made clear when we become acquainted with the Nernst Theorem.

The Two Equilibrium Constants of a Gaseous Reaction and the Variation of one of them with Pressure.

In deducing the expression (the van 't Hoff Isotherm),

$$A = RT\log K - RT\Sigma\nu\log C$$

we have regarded the concentrations (in terms of which K is measured) as the number of gram-molecules per liter, *i.e. volume* concentration terms. In carrying out the reversible work process from reactants at an arbitrary concentration to resultants also at arbitrary concentrations via the equilibrium box, the work term A being a maximum is identical with the decrease of the free energy of the system due to the process. The decrease in free energy is independent of the path followed being dependent only upon the initial and final states. That is, the term A is independent of the actual conditions which obtain in the equilibrium box. That is, A is independent of the absolute values of the concentrations of the various gases in the box provided only that the mixture is in equilibrium. Neither does A depend upon the total pressure exerted by the constituents of the box. That is, K itself is independent of the pressure, *i.e.* the total pressure of the gaseous system to which K refers, although, of course, K varies with the temperature.

Again consider the general reaction—

$$\nu_1 A_1 + \nu_2 A_2 + \text{etc.} = \nu'_1 A'_1 + \nu'_2 A'_2 + \text{etc.}$$

and let us express the concentrations as molar fractions, *i.e.* as the ratio of the number of molecules of A_1, say, to the total number of molecules present. Suppose there are n_1 molecules of A_1, n_2 molecules of A_2, n'_1 molecules of A'_1, and n'_2 molecules of A'_2 etc. Denoting each of these molecular concentration terms by γ, we have—

$$\text{Concentration of } A_1 = \gamma_1 = \frac{n_1}{n_1 + n_2 + n'_1 + n'_2 + } = \frac{n_1}{\Sigma n}$$

$$\text{“ “ } A_2 = \gamma_2 = \frac{n_2}{\Sigma n}$$

$$\text{Concentration of } A'_1 = \gamma'_1 = \frac{n_1}{n_1 + n_2 + n'_1 + n'_2 +} = \frac{n'_1}{\Sigma n}$$

$$\text{,,} \qquad \text{,,} \quad A'_2 = \gamma'_2 \qquad = \frac{n'_2}{\Sigma n} \text{ etc.}$$

The volume concentration of A_1 is $c_1 = n_1/V$; similarly $c_2 = n_2/V$, etc. It is evident that $\gamma_1 = n_1 . V/V\Sigma n = c_1 . V/\Sigma n$.

Also
$$V = \frac{RT}{p} . \Sigma n.$$

Therefore,

$$\gamma_1 = c_1 . RT/p$$
$$\gamma_2 = c_2 . RT/p, \text{ etc.,}$$

where p is the total pressure in the equilibrium box.
Hence

$$\frac{\gamma'_1{}^{\nu'_1} . \gamma'_2{}^{\nu'_2} .}{\gamma_1{}^{\nu_1} . \gamma_2{}^{\nu_2} .} = \frac{c'_1{}^{\nu'_1} . c'_2{}^{\nu'_2} .}{c_1{}^{\nu_1} . c_2{}^{\nu_2} .} . \left(\frac{RT}{p}\right)^{\nu'_1 + \nu'_2 + \ldots - \nu_1 - \nu_2 - \ldots}$$
$$= K\left(\frac{RT}{p}\right)^{\Sigma\nu' - \Sigma\nu}.$$

Hence the quantity $\frac{\gamma'_1{}^{\nu'_1} . \gamma'_2{}^{\nu'_2} .}{\gamma_1{}^{\nu_1} . \gamma_2{}^{\nu_2} .}$ is also a constant, say K′, which depends, however, upon the total pressure in the box as well as upon the temperature. We have now to find how K′ varies with the total pressure. Writing down the expression—

$$K' = K\left(\frac{RT}{p}\right)^{\Sigma\nu' - \Sigma\nu}$$

and taking logarithms, we obtain—

$$\log K' = \log K + (\Sigma\nu' - \Sigma\nu) \log RT - (\Sigma\nu' - \Sigma\nu) \log p.$$
$$\therefore \left(\frac{\partial \log K'}{\partial p}\right)_T = - \frac{\Sigma\nu' - \Sigma\nu}{p}.$$

If $\mathbf{V}$ is the total volume of $\nu_1 + \nu_2 +$ etc., molecules of reactants, and $\mathbf{V}'$ is the volume of $\nu'_1 + \nu'_2 +$ etc., molecules of resultants, then—

$$p\mathbf{V} = \Sigma\nu . RT$$
$$p\mathbf{V}' = \Sigma\nu' . RT.$$
$$\therefore p(\mathbf{V}' - \mathbf{V}) = (\Sigma\nu' - \Sigma\nu) . RT.$$
$$\therefore \left(\frac{\partial \log K'}{\partial p}\right)_T = - \frac{(\mathbf{V}' - \mathbf{V})}{RT}.$$

This important relation gives the variation of K′ (defined in terms of molar fractions or "molecular" concentration terms) with the total pressure exerted upon the system. The term $-(\mathbf{V}' - \mathbf{V})$ denotes the *decrease* in volume accompanying the reaction when the stoicheiometric quantities ν_1, ν_2, etc., are transformed into the stoicheiometric quantities ν'_1, ν'_2 etc. If $\Sigma\nu' = \Sigma\nu$, that is, if the reaction does not involve a change in the total number of molecules and there is therefore no change in volume, then in such a case K′ is independent of the pressure. K is always independent of p.

The Law of Mass Action and the Van 't Hoff Isochore from the point of view of Entropy.

Suppose we have a gaseous system consisting of the substances A, B, C, and D in which the reaction $A + B = C + D$ can occur. Suppose the total entropy of the system in the equilibrium state is S. We have seen already that the total entropy is the sum of the separate entropies of the constituents. That is—

$$S = S_A + S_B + S_C + S_D.$$

If we imagine a small virtual change in the system whereby the reaction occurs to a slight extent, A and B disappearing and C and D being formed, then the corresponding change in the total entropy is given by—

$$\delta S = -\delta S_A - \delta S_B + \delta S_C + \delta S_D.$$

Let us suppose that each substance is a perfect gas. Then for the substance A we can write—

$$S_A = C_{vA} \log T + R \log V_A + S_0$$

or $$S_A = C_{vA} \log T - R \log C_A + S_0$$

where C_A is the concentration of A expressed as a reciprocal of the volume which contains one gram-molecule. It was shown in Chap. II that as a criterion of equilibrium we can make use of the expression $(\delta S) = 0$, *i.e.* the entropy of an isolated system is a maximum at the equilibrium point, and if any very small possible change be imagined to occur in the system the change in entropy is zero. For the equilibrium system considered this relation takes the form—

$$-(\delta S_A) - (\delta S_B) + (\delta S_C) + (\delta S_D) = 0.$$

If T is constant $C_v \log T$ is constant and therefore $\delta C_v \log T = 0$. Similarly the integration constant S_0 is a constant and consequently $S_0 = 0$.

Hence at a given temperature the equilibrium expression just given is equivalent to—

$$+ R\delta \log C_A + R\delta \log C_B - R\delta \log C_C - R\delta \log C_D = 0$$

or $$\delta \log \frac{C_A \times C_B}{C_C \times C_D} = 0,$$

or $$\delta \log \frac{C_C \times C_D}{C_A \times C_B} = 0$$

or $$\log \frac{C_C \times C_D}{C_A \times C_B} = \text{a constant},$$

or $$\frac{C_C \times C_D}{C_A \times C_B} = K$$

where K is the equilibrium constant of the reaction. The concept of entropy leads therefore to the Law of Mass Action (as expressed in the equilibrium constant) for a system consisting of *perfect* gases.

In the above we have been considering a small virtual change at the equilibrium point in which the entropy remained unchanged. Let us

now consider a real change of the equilibrium system whereby the entropy alters by a definite amount. Suppose that one mole of A reacts in a reversible manner with one mole of B to give rise to one mole of C and one mole of D. The change in the total entropy of the system is Q_p/T where Q_p is the heat of the reaction at constant pressure. Note that Q_p denotes heat absorbed. This must be equal to the sum of the changes of the separate entropies of the constituents. Denote the change in entropy of the gas A by S_1, change in entropy of B by S_2, and so on. Since A and B disappear their entropy decreases. The total change is therefore given by—

$$-S_1 - S_2 + S_3 + S_4 = Q_p/T.$$

But
$$S_1 = C_{vA} \log T - R \log C_A + S'$$

where each of the terms refer to one gram-molecule of the gas. Similar expressions hold for the other entropies. Hence the preceding equation may be written—

$$(C_{vC} + C_{vD} - C_{vA} - C_{vB}) \log T - R \log C_C \cdot C_D/C_A \cdot C_B + \Sigma S' = Q_p/T,$$

or
$$\log C_C \cdot C_D/C_A \cdot C_B = -Q_p/RT + \frac{C_v}{R} \log T + \Sigma S'/R.$$

The right-hand side is the complete expression for the equilibrium constant K in the case of a reaction between perfect gases. In the case of a perfect gas, however, the internal energy and therefore $C_v \log T$ is independent of the volume and therefore of the pressure. Hence K as defined above (in terms of volume concentrations) is independent of the pressure, a result which we have already obtained by a consideration of the van 't Hoff isotherm. K is now seen to be explicitly a function of T. If T be kept constant the terms on the right-hand side are constant, and hence for the system considered, the expression on the left is likewise constant, *i.e.* the equilibrium constant.

If we denote $C_C \cdot C_D/C_A \cdot C_B$ by K, and differentiate the above expression with respect to temperature, we obtain—

$$\frac{d \log K}{dT} = \frac{Q_p}{RT^2} - \frac{1}{RT} \cdot \frac{dQ_p}{dT} + \frac{\Sigma C_v}{RT} + \frac{\log T}{R} \cdot \frac{d\Sigma C_v}{dT}.$$

But the specific heat of a perfect gas is independent of the temperature

Hence $\frac{d\Sigma C_v}{dT} = 0$ and the expression becomes—

$$\frac{d \log K}{dT} = \frac{Q_p}{RT^2} - \frac{1}{RT} \frac{dQ_p}{dT} + \frac{\Sigma C_v}{RT}.$$

Further, from Kirchhoff's equation (Chap. I) we have—

$$\frac{dQ_p}{dT} = \Sigma C_p = \Sigma(C_v + R).$$

Therefore
$$\frac{d \log K}{dT} = \frac{Q_p}{RT^2} - \frac{\Sigma(C_v + R)}{RT} + \frac{\Sigma C_v}{R}$$
$$= \frac{Q_p}{RT^2} - \frac{\Sigma R}{RT} = \frac{Q_p - \Sigma RT}{RT^2}.$$

The term ΣRT denotes the work done by expansion of the system. [In the particular case chosen there is no change in the total number of molecules as a unit of the reaction, and hence there is no expansion, *i.e.* $\Sigma RT = 0$. In general, however, ΣRT will possess a positive or negative value.] In general therefore—

$$Q_p = Q_v + \Sigma RT$$

where Q_v is the heat absorbed in the reaction when the reaction occurs at constant volume. Hence—

$$\frac{d \log K}{dT} = \frac{Q_v}{RT^2}$$

which is van 't Hoff's isochore obtained by a consideration of the entropy of the system.

In the above, K has been expressed in terms of volume concentrations (gram-molecules per liter). Let us now express it in terms of partial pressures. For the partial pressure p_A of the gas A in the equilibrium state we have—

$$p_A = RTC_A$$

and therefore

$$\log p_A = \log C_A + \log RT.$$

Hence

$$\log \frac{p_C \cdot p_D}{p_A \cdot p_B} = \log \frac{C_C \cdot C_D}{C_A \cdot C_B} + \Sigma \log RT.$$

[As already pointed out ΣRT in this case is zero; in general it is not zero.]

It follows, therefore, if we denote the left-hand expression by K_p that—

$$\frac{d \log K_p}{dT} = \frac{d \log K}{dT} + \frac{\Sigma}{T}$$

$$= \frac{Q_v + \Sigma RT}{RT^2} = \frac{Q_p}{RT^2}.$$

In the above case (no change in the total number of molecules) $Q_v = Q_p$ and $K_p = K$. In a reaction in which the total number of molecules changes as a result of the reaction, Q_v differs from Q_p, and K_p from K. K has been shown to be independent of the total pressure of the system, and as $\log K_p$ only differs from $\log K$ by a term $\Sigma \log RT$, which is independent of pressure, it follows that K_p is likewise independent of pressure. K_p is not to be confused with K′ dealt with in the preceding section, in which K′ is defined in terms of "molecular concentrations" or molar fractions and does vary with the pressure.

CHAPTER VI.

Chemical equilibrium in homogeneous systems—Dilute solutions—Applicability of the Gas Laws—Thermodynamic relations between osmotic pressure and the lowering of the vapour pressure, the rise of boiling point, the lowering of freezing point of the solvent, and change in the solubility of the solvent in another liquid—Molecular weight of dissolved substances—Law of mass action—Change of equilibrium constant with temperature and pressure.

The Applicability of the Gas Laws to Dilute Solutions.

As already pointed out (in Vol. I.), we owe to van 't Hoff the discovery of the close connection between the behaviour of gases and the behaviour of substances in the dissolved state. The quantitative connection between the two only holds for dilute solutions, an ideally dilute solution being one in which further addition of solvent does not cause any heat effect (heat of dilution). In this chapter the thermodynamic proof of the applicability of the gas law expression $PV = RT$ to the osmotic pressure-concentration relations of a dissolved substance will be given. It is important to notice that this cannot be done *simply* on thermodynamic grounds. It is necessary to assume the truth of the experimental law discovered by Henry, namely, that the concentration of gas dissolved in a liquid is proportional to the pressure of the gas at the given temperature. As has been shown in Vol. I., this law holds in a large number of cases, *i.e.* in those cases in which the molecular condition of the solute is the same in the gaseous and dissolved states respectively. Henry's Law does not hold in the above simple form for substances which polymerise or dissociate electrolytically when dissolved in a solvent. This has been dealt with at some length in Vol. I. For our present purpose, therefore, we shall only consider the case of a gas which dissolves "normally" and obeys Henry's Law accurately. To deduce the gas law for the *dissolved* gas it is necessary to go through an isothermal reversible cycle and equate the sum of all the work terms to zero. To carry this process out it is necessary to postulate the existence of semi-permeable membranes, it being a matter of no consequence what may be the mechanism of the semi-permeability.[1] Naturally we are only dealing with ideal or limiting conditions, none of which can ever be realised in practice. The proof that the osmotic pressure of a dissolved substance is quantitatively identical with the gas pressure which the substance would exert if it were in the gaseous state at the same temperature and at the same concentration (or dilution or volume), is that given by van 't Hoff in his Lectures (Part II.), and is due partly to van 't Hoff, partly to Lord Rayleigh, and partly to Donnan.

[1] A simple proof that the magnitude of the osmotic pressure is independent of the nature of the semi-permeable membrane is given by Ostwald (*Lehrbuch d. allg. Chem.* I., 662).

The Thermodynamic Proof by means of a Reversible Cycle.

Consider a cylinder, such as that shown in Fig. 19, containing a quantity of gas in equilibrium with a solution of the gas. The vapour pressure of the solvent is supposed to be negligible as compared with that of the gas. The solution is separated from the undissolved gas by the membrane *bc*, which only permits the gas to pass through but not the solvent, say water. The walls *ab* and *cd* are in contact with pure solvent and are permeable to the solvent but impermeable to the solute (dissolved gas). The system being in equilibrium, let us suppose that p is the pressure of the gas (in the gas phase), v is the molecular volume or volume of 1 gram-mole of the gas at pressure p, and similarly let P be the osmotic pressure and V the molecular volume of the solute, *i.e.* dissolved gas in equilibrium with the gas at p. The concentration of the solute is c where $c = \frac{1}{V}$. Henry's Law states that $c \propto p$. The ends of the cylinder are closed by movable impermeable pistons. Suppose both pistons to be moved upwards so that 1 gram-mole of solute is transferred from the liquid solution to the gaseous state. That is, the upper piston moves through a volume v, the work done by the system reversibly (maximum work) being pv. Simultaneously the external surroundings push the lower piston up through a volume V (the solvent passing out through *ab* or *cd*; the level of liquid remaining of course at *bc*). The work done upon the system is here – PV, the negative sign denoting work done *on* the system. Hence the net work done by the system is pv – PV. The first process is now completed.

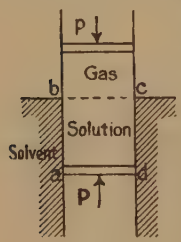


Fig. 19.

The second process consists in restoring the gram-mole of gas to the solution by another reversible isothermal path. To do so we first of all imagine the gram-mole of gas at volume v and pressure p isolated from the rest of the system by pushing across a weightless, frictionless shutter (this process involves no work in the ideal case), and we then suppose the isolated gas to be reversibly expanded to an extremely great dilution practically infinite volume, namely v_∞. The maximum work done by the system in this process is—

$$\int_v^{v_\infty} p dv = \mathrm{RT} \int_v^{v_\infty} \frac{dv}{v} = \mathrm{RT} \log \frac{v_\infty}{v}.$$

This gas may now be brought into contact with a volume V of water, this process being reversible in the limiting case in which the dilution of the gas is practically infinite, for under these circumstances the water would not absorb any of the infinitely dilute gas, *i.e.* the process of absorption would go infinitely slowly and therefore reversibly. Suppose the piston to be lowered gradually until the gas, *i.e.* 1 mole, is entirely dissolved in the volume V of solvent. The positive work done by the surroundings is equivalent to—

$$-\int_{v=0}^{v_\infty} p_1 dv_1$$

the negative sign denoting that work is reckoned as done by the system. During the compression, however, p_1 is not related to v_1 by the usual expression

$$p_1 v_1 = RT$$

if R be taken as referring to 1 *mole*. p_1 is really smaller than this (at any stage of the process of dissolving the gas) because a portion of the gas has already disappeared from the gas phase and has gone into solution. This part which has dissolved will evidently amount to 1 gram-mole when the pressure exerted by the piston is p (for 1 mole of gas in V volume of solvent is the original concentration of dissolved gas which we assumed to be in equilibrium with a gas phase at pressure p). When the pressure exerted by the piston is p_1, ($p_1 < p$) the amount of gas which has gone into solution must be the fraction $\frac{p_1}{p}$ of 1 gram-mole, that is if Henry's Law regarding the direct proportionality between quantity of dissolved gas and pressure be taken as true. The quantity remaining undissolved in the gaseous state at p_1 is therefore $\left(1 - \frac{p_1}{p}\right)$, and this is the mass of gas to which we must apply the gas equation. That is, at any stage—

$$p_1 v_1 = \left(1 - \frac{p_1}{p}\right)RT = RT - p_1 v$$

or

$$p_1 = \frac{RT}{v + v_1}.$$

We can use this relation between p_1 and v_1 to integrate the expression—

$$-\int_0^{v_\infty} p_1 dv_1.$$

Thus—

$$-\int_0^{v_\infty} p_1 dv_1 = -RT\int_0^{v_\infty} \frac{dv_1}{v_1 + v} = -RT \log \frac{v_\infty + v}{v}.$$

Neglecting v compared to v_∞ we get the work of dissolving 1 mole of gas reversibly and isothermally in a volume V of solvent to be—

$$-RT \log \frac{v_\infty}{v}.$$

Now we have got the gas back into the solvent at the same concentration as that of the original solution from which we had taken it initially. To all intents and purposes this is identical with bringing the gas back into the original solution itself, for we have simply to bring this volume V of solution into contact with the original solution when they will mix, there being no work process involved in this since both systems are one and the same. Hence the cycle is complete, and by the Second Law

of Thermodynamics the nett work done in an isothermal reversible cycle is zero. That is, the work terms—

$$pv - PV + RT \log \frac{v_\infty}{v} - RT \log \frac{v_\infty}{v} = 0,$$

or $$pv = PV$$

but $$pv = RT.$$

$$\therefore PV = RT$$

That is, the osmotic pressure obeys the generalised gas law, which includes Boyle's Law, Gay-Lussac's, and the Avogadro Hypothesis. It will be observed that the "R" is numerically identical with the R of the perfect gas equation. That is, the osmotic pressure of a dilute solution is related to the molecular volume, or the inverse of this the molecular concentration *quantitatively* as the pressure of a perfect gas is related to the volume. For substances in dilute solution R = 1·985 calories per gram-mole. It may be noted that in the particular case in which V = *v* the osmotic pressure is identical with the gas pressure.

The deduction just given, which is based on a thermodynamic cycle, and also on the validity of Henry's Law, proves that the osmotic pressure obeys Boyle's and Gay-Lussac's Laws, and is in agreement with the Avogadro Hypothesis.

The experimental evidence that the osmotic pressure of dilute solutions is identical with gas pressure is furnished by the work of Morse and Fraser and their collaborators, to which reference has already been made in the chapter on solution in Vol. I. As a corollary to the proof which has just been given, it should be mentioned that if it is assumed that the osmotic pressure of a dissolved gas does obey the gas laws, then it is possible by means of a thermodynamic cycle to deduce Henry's Law of Absorption. (Compare, for example, Sackur's *Thermochemistry and Thermodynamics*, English Ed., p. 273, in which is given the deduction of the Distribution Law of which Henry's Law is a particular case.)

The applicability of Henry's Law has recently been investigated over a considerable pressure range by Sander (*Zeit. für physik. Chem.*, **78**, 513, 1912), and by Sackur and Stern (*Zeit. für Electrochemïe*, **18**, 641, 1912), the object being to see what concentration values are reached both in the gaseous phase and in the solution before the simple gas law breaks down. Sackur and Stern consider they have shown the very interesting fact, that in the case of carbon dioxide partly dissolved in various organic liquids the gas law breaks down for the gas phase much sooner than it breaks down for the *same substance* in the solution. In other words, we can consider that a solution is functioning as an "ideal solution" to higher osmotic pressures, than is the case with the gas itself in equilibrium with this solution. In the following table are given some of the results of Sackur and Stern, on the absorption coefficient; and in order to be able to work up to considerable concentrations without introducing very high pressures which might give rise to some experimental difficulties,

measurements were made at low temperatures, – 78° C. and – 59° C., since the solubility of the gas is greater the lower the temperature. The distribution coefficient can be expressed in two ways.

Bunsen's Definition.—The coefficient k' denotes the quantity of CO_2 in cubic centimeters at 0° C. and at the pressure of the experiment absorbed by 1 gram of the liquid.

Ostwald's Definition.—The coefficient k is the ratio of the concentration of the CO_2 in the solution and in the gas space. (This is obtained from the k' value by employing, in addition, data for the density of the solution.) Both k and k' are given in the following table.

ABSORPTION COEFFICIENT OF CO_2 GAS IN VARIOUS SOLVENTS.

I.—Temperature – 78° C.

Solvents—	Methyl Alcohol.		Acetone.	
Pressure of Gas in mm. of Mercury.	k'.	k.	k'.	k.
50	194·0	120·5	311·0	196·6
100	195·0	119·6	322·0	198·1
200	202·9	120·1	344·5	201·5
400	221·5	122·2	400·0	208·8
640	—	—	487·0	215·7
700	260·0	126·8	—	—

II.—Temperature – 59° C.

Solvents—	Ethyl Alcohol.		Acetone.		Methyl Acetate.	
Pressure of Gas in mm. of Mercury.	k'.	k.	k'.	k.	k'.	k.
100	40·85	27·3	97·8	67·2	94·3	75·8
200	41·00	27·2	101·2	68·0	98·45	77·1
400	42·35	27·65	106·6	69·2	103·6	77·6
700	44·15	28·1	118·8	72·8	112·9	79·0

It will be seen from these tables that Henry's Law, when expressed in terms of the Ostwald coefficient k, holds over a much wider pressure range than when expressed in terms of k'. Up to 200 mm. k remains constant within the limits of experimental error, and it will be observed, that at the same time the magnitude of the coefficient shows that the concentration of the dissolved gas becomes very considerable. Using an empirical formula, Sackur and Stern have calculated with the aid of these absorption coefficients the values of the osmotic pressure of the

various solutions, and hence the concentration. To indicate the order of concentration obtained we may mention that the solubility of CO_2 at $-78°$ C. in methyl alcohol in gram-moles per litre, under 50 mm. pressure, is 0·495 (*i.e.* nearly half molar), under 400 mm. the concentration is 4·02 (*i.e.* approx. 4 molar), and under 700 mm approx. 7 molar. It must be remembered, of course, that in the case of non-volatile solutes such as sugar in aqueous solution the simple gas laws break down at much lower concentrations. As already mentioned, the limit up to which a solution can be regarded as accurately ideal is about $\frac{1}{10}$N.

Thermodynamic Relations between the Osmotic Pressure of Dilute Solutions and other Properties of such Solutions.

I.—*The Relation between Osmotic Pressure and Lowering of Vapour Pressure of the Solvent due to the presence of a Solute.*

Incidentally it may be pointed out that by the aid of the Le Chatelier and Braun principle one can predict that the vapour pressure (of the solvent, of course) over a solution containing a non-volatile solute is less than the vapour pressure over the pure solvent itself at the same temperature. Thus, consider the solvent alone in equilibrium with its vapour. Dissolve some non-volatile substance in the liquid. According to the principle the system tends to remain in its former state, *i.e.* it tends to lower the concentration of the solute as far as possible since it will thereby be approximating to the state of pure liquid. It effects this by causing some of the vapour to be condensed, thereby making the vapour more dilute, and therefore lowering the vapour pressure.

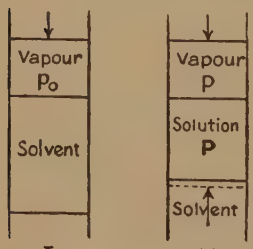


Fig. 20.

To show the connection between the lowering of vapour pressure due to the solute, and the osmotic pressure of the solution, we imagine the following isothermal reversible cycle carried out. In one vessel there is a solvent in contact with its own vapour at pressure p_0 (Fig. 20). Vapour can be removed by means of the piston. In a second vessel there is a solution of a non-volatile solute, the osmotic pressure being P, and the vapour pressure p when $p < p_0$. Pure solvent can be removed from the second vessel by pressing in the lower piston, which is fitted with a semi-permeable membrane, *i.e.* one allowing solvent to pass through but not solute. The temperature of both vessels is the same. The cycle consists in evaporating a certain quantity of solvent from the first vessel, and adding it to the second by the upper piston, and removing it again by the lower piston, and finally transferring it to the first vessel once more.

The expression for the isothermal reversible transfer of given mass of solvent from vessel I. to vessel II. by distillation involves the familiar

three-stage work process, and is given by the term $-\int_{p_0}^{p} v\,dp$, or $\int_{p}^{p_0} v\,dp$. Supposing the vapour obeys the gas laws, then the work done by the system in the transfer of 1 mole is $RT \log \frac{p_0}{p}$. If the quantity is only dx moles, then the work done is—

$$dx\ RT \log \frac{p_0}{p}.$$

The quantity dx is now in the solution. By using the lower piston of vessel II. one can squeeze out reversibly a volume dv of solvent corresponding to the mass dx, the work done upon the system being $P dv$, where P is the osmotic pressure against which the piston was moved. For such a small volume change as dv the value of the osmotic pressure remains sensibly constant. The isolated volume dv is now added without work of any kind to the first vessel, and the initial condition of things is once more restored. Since the process has been carried out isothermally and reversibly, the Second Law of Thermodynamics states that the sum of all the work terms is zero. Reckoning work done *by* the system as positive and work done *on* the system as negative, the Second Law leads to the relation—

$$dx RT \log \frac{p_0}{p} + (-P dv) = 0$$

or

$$dx RT \log \frac{p_0}{p} = P dv.$$

Now $m\frac{dx}{dv}$ = density of the liquid solvent = ρ, where m is the molecular weight of the solvent *as vapour*.

$$\therefore \log \frac{p_0}{p} = \frac{Pm}{\rho RT}$$

which is the relation required.

In a dilute solution $P = RTc$, where c is the molar concentration of the solution, and therefore—

$$\log \frac{p_0}{p} = \frac{cm}{\rho}, \text{ or } \log \frac{p_0}{p} \propto c$$

which is the accurate form of Raoult's Law based on thermodynamics. If the difference between p and p_0 is small, one may substitute $\frac{p_0 - p}{p}$ in place of $\log \frac{p_0}{p}$,[1] and hence obtain—

$$\frac{p_0 - p}{p} = \frac{mP}{\rho RT}$$

[1] The term $\log p_0/p$, in which $p_0 > p$ can be written thus:—

$$\log \left(1 + \frac{p_0 - p}{p}\right).$$

Further the expression $\log (1 + x)$ becomes in the limit (when x is small) simply

which is the approximate relation between P and $(p_0 - p)$ already deduced in Vol. I. on kinetic grounds. Some numerical illustrations are given there.

II.—*The Lowering of Solubility of one Liquid in another owing to the Presence of a Solute in one of the Liquids.*

Take the case of a system consisting of water and ether, the lower layer being a solution of ether in water. If one adds to the upper ether layer a substance soluble *only* in ether and not in water, it will be found that the presence of the solute in the upper layer has caused the concentration or solubility of the ether in the water layer to decrease. The behaviour is quite analogous to the lowering of vapour pressure discussed in the previous section, if we imagine the water layer to take the place of the vapour space and the concentration of the ether in the water to correspond to the vapour pressure of the solvent in the previous case. We can thus directly apply the thermodynamically deduced formula—

$$\log \frac{p_0}{p} = \frac{Pm}{\rho RT}$$

to the present case if we use s for p and s_0 for p_0, where s is the solubility of the ether in the water layer when the solute is present in the ether layer; s_0 the solubility of the ether in the water layer before the solute has been added. That is—

$$\log \frac{s_0}{s} = \frac{Pm}{\rho RT}$$

where P is the osmotic pressure of the solute in the ether layer, ρ the density of liquid ether and R and T have the usual significance.

III.—*Relation between the Osmotic Pressure* P *of the Solute and the rise of Boiling Point* ΔT *of the Solvent due to the presence of the* (*Non-volatile*) *Solute.*

This relation can be obtained by means of a cycle which differs, however, from that employed in I., in that the cycle is not carried throughout at *the same temperature*. Consider the two vessels figured (Fig. 21). That containing the solution (vessel I.) is at temperature T_2, at which temperature the solution boils, *i.e.* the vapour pressure is 1 atmosphere. The vessel II. contains solvent also boiling, *i.e.* vapour pressure is equal to 1 atmosphere and the temperature is T_1. T_1 is less than T_2. We shall denote the difference between them by ΔT.

equal to x itself. Hence in the case of a very dilute solution the above expression reduces to $(p_0 - p)/p$. Further, since the solution is dilute p is very nearly equal to p_0, so that, as a first approximation we may write—

$$\frac{p_0 - p}{p} = \frac{p_0 - p}{p_0}.$$

The cycle is as follows :—

(1) Starting with vessel I., let us suppose a quantity dx grams of solvent is vaporised from the solution at temperature T_2. The heat which is taken in from the surroundings is the latent heat. If L is the latent heat per gram of solvent, the heat taken in for mass dx is Ldx. At the same time the reversible work pdv is done by the system.

(2) The quantity dx of vapour is now cooled to T_1, *i.e.* through an interval ΔT. If k is the specific heat of the vapour, the amount of heat given out is a very small quantity $kdx\Delta T$.

(3) The vapour is now condensed in vessel II. at T_1, reversibly, the work done upon the system being very nearly $-pdv$, so that the work terms expressed in (1) and (3) balance one another. Heat is given out in an amount somewhat less than Ldx.

(4) The quantity dx now in the form of liquid is separated without work from the vessel II. by sliding a shutter across. The small mass of liquid is raised to the temperature T_2. The heat added in doing this is $k'dx\Delta T$, where k' is the specific heat of the liquid. Although in general k and k' differ considerably, the heat quantities in the two cases (Stages (2) and (4)) are so small that they might be neglected, when compared to Ldx, particularly since they are opposite in sign.

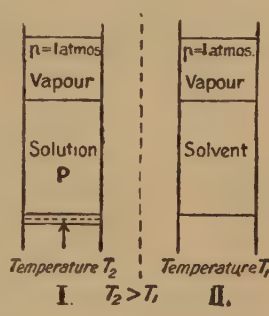


FIG. 21.

(5) Finally, at temperature T_2, add the mass dx (which occupies the volume dV) of liquid solvent to the solution reversibly, the osmotic work being PdV. This is the only nett work of the process. The cycle is now completed. For the sake of making the cycle clear all the steps have been described in detail. For the purpose of using the Second Law expression, $dA = Q\frac{dT}{T}$, where dA is the external work done, and Q the heat taken in at the high temperature T, it is only necessary to take into account the nett external work done, namely PdV in the above cycle, and connect it with the Q which is evidently represented by the term Ldx. The Second Law expression in the present instance becomes therefore—

$$PdV = (Ldx)\frac{\Delta T}{T_2}.$$

Putting—

$$\frac{dx}{dV} = \rho$$

where ρ is the density of the solvent, we obtain—

$$P = \frac{L\rho\Delta T}{T_2}.$$

This expression connects the osmotic pressure of the solution with the rise of boiling point ΔT. Since the solution is dilute, we can write in general—

$$P = RTC$$

which for temperature T_2 becomes $P = RT_2C$, where C is the concentration of the solute.

Hence $$C = \frac{L\rho\Delta T}{RT^2_2}.$$

This is the theoretical basis for the Raoult generalisation.

IV.—*The Relation between Osmotic Pressure* P *and the lowering of Freezing Point* ΔT *of the Solvent due to the presence of the Solute.*

We imagine a cycle very similar to the previous one carried out. Consider two vessels (Fig. 22) I. and II. Vessel I. contains solvent (water, say) in equilibrium with ice at the freezing point T_0. The vessel II. contains an aqueous solution which is also in equilibrium with ice at the temperature T lower than T_0 by the amount ΔT. The osmotic pressure in II. is P.

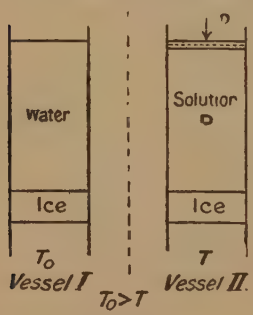


FIG. 22.

1st Stage.—Suppose a very small quantity *dx* grams of ice is withdrawn from vessel I. at T_0. No work is done in this process, equilibrium being established throughout. Now suppose the ice is melted. If L is the latent heat of fusion per gram of ice, the quantity of heat taken in by the system from the surrounding at T_0 is Ldx. In this process there is a very small amount of work done upon the system owing to the change in volume of *dx* on fusion. This, as will be seen in (3), is practically neutralised by a similar work term in the opposite sense at temperature T.

2nd Stage.—Suppose the mass *dx* of liquid water at T_0 occupies a volume *d*V. Cool this from T_0 to T. If *k* is the specific heat of water, the heat given out (a small quantity) is $kdx\Delta T$. The change in the volume of the liquid due to the temperature change may be neglected. The volume *d*V of water is now, by means of a semipermeable membrane, reversibly and isothermically added to the solution at the temperature T. The maximum work done by the system is P*d*V.

3rd Stage.—Suppose a quantity *dx* of water is frozen out of the solution in vessel II. A quantity of heat is given out in a somewhat less amount than that taken in at the fusion process in vessel I. The system at the same time expands in the solidification, *i.e.* does work against the surroundings, and this is balanced by the small work term referred to in Stage 1.

4th Stage.—The mass *dx* of ice at T is isolated without work from vessel II., and is raised in temperature to T_0. If *k'* is the specific heat

of ice, the heat absorbed is $k'dx\Delta T$. This is a small quantity, and is practically balanced by the opposite term in Stage 2. The quantity dx of ice at temperature T_0 is now added without work to vessel I., and the cycle is completed. Applying the Second Law, we get—

$$dA = Q\frac{dT}{T}$$

or

$$PdV = Ldx\frac{\Delta T}{T_0}.$$

Putting—

$$\frac{dx}{dV} = \rho$$

the density of the liquid water, we have the equation—

$$P = \frac{L\rho\Delta T}{T_0}.$$

If the solution is dilute, and therefore obeys the Gas Law—

$$P = RT_0C$$

or

$$C = \frac{L\rho\Delta T}{RT_0^2}.$$

This expression has exactly the same form as that obtained for the rise of boiling point. It is the thermodynamical basis of the Raoult generalisation regarding the concentration of a solution and the lowering of freezing point.

Note that ΔT is a positive term in the case of the effect on the boiling point, but a negative term in the case of the effect on the freezing point.

Methods for Determining Molecular Weight of Dissolved Substances.

The relations (I.-IV.), as well as direct measurements of osmotic pressure, can be employed to obtain the molecular weight of a given dissolved substance.

Thus, suppose that in a volume V of solvent we dissolve x grams of solute. If M in grams is the molecular weight of the solute in the dissolved state, $\frac{x}{M}$ is the number of gram-moles of solute present in volume V. The concentration in moles per cubic centimetre is thus $\frac{x}{MV}$. Now applying the Gas Law to the solution—

$$P = RTC$$

or

$$P = \frac{RTx}{MV}, \text{ or } M = \frac{RTx}{PV}.$$

The First Method of obtaining the molecular weight of a solute is to measure directly, as Pfeffer did, the osmotic pressure P when a mass x is dissolved in a volume V at temperature T. The numerical value to be

assigned to R depends on the units used. Thus if PV be represented in calories, R will be 1·98. If, as is more usual, P be measured in atmospheres and V in liters (PV in liter-atmospheres), then R has the value 0·0821. When P is known, M can be calculated by the above relation.

The Second Method is based on the lowering of the vapour pressure by the non-volatile solute. The formula deduced is—

$$\log \frac{p_0}{p} = \frac{Pm}{\rho RT}$$

where m = molecular weight *of solvent.*

Substituting $$P = \frac{RTx}{MV}$$

we have the equation $$M = \frac{xm}{\rho V} \log \frac{p_0}{p}.$$

The determination of the molecular weight of solutes by the lowering of vapour pressure could scarcely be regarded as one of the most convenient methods until quite recently, A. W. C. Menzies (*Zeitsch. fur Phys. Chem.*, **76**, 231, 1911) has described a very convenient form of apparatus in which the lowering of pressure is measured by a column of the solution itself, and which allows accurate determinations of molecular weights being carried out rapidly. The following table is an illustration of the accuracy obtainable :—

Solvent : *Water.* Solute : *Sodium Chloride.*

Mass of Substance in Grams.	Volume of Solution in c.cs.	$(p_0 - p)$ in mm. of Solution.	Molecular Weight Found.
0·351	38·0	56·2	32·5
0·579	40·4	84·4	33·3
0·488	33·8	84·4	33·4
Solvent : *Benzene.* Solute : *Naphthalene.*			
0·3115	48·1	60·1	128·6
0·5118	49·1	105·2	127·5
0·3237	46·1	65·2	128·0
0·5092	46·8	101·6	127·3
			Theoretical 128·0

Menzies draws the following comparison between this method and the boiling point rise method :—

"The present method is capable of greater accuracy, since for a pressure lowering amounting to about 40 mm. the change in boiling point is only 0·1°."

The Third Method of obtaining the molecular weight of dissolved substances is that depending on the lowering of solubility. In the formula—

$$\log \frac{s}{s_0} = \frac{Pm}{\rho RT}$$

we substitute the value of P in terms of RT, MV, and x. None of these methods has come into such universal use as those depending on the rise of boiling point and the lowering of freezing point due to the classic work of Beckmann.

The Fourth Method.—The lowering of freezing point. The expression

$$P = \frac{L\rho\Delta T}{T_0}$$

may be transformed by writing $P = RT_0\frac{x}{MV}$ into—

$$M = \frac{RT_0^2 x}{VL\rho\Delta T}.$$

It will be observed that for a given solvent the expression $\frac{RT_0^2}{L\rho}$ is a constant (Raoult's constant).

Putting this equal to k, we obtain—

$$M = k\frac{x}{V\Delta T}.$$

Van 't Hoff was the first to calculate k on the above thermodynamic basis. For the case of water—

L = latent heat of fusion = 80 calories per gram;
R = 1·985 calories per degree;
T_0 = 0° C. = 273° abs.;
ρ = 1 (approx.);

$$\therefore \frac{RT_0^2}{L\rho} = 1863° = k.$$

For the special case in which x is chosen equal to M and V = 1 c.c., it is evident that ΔT = 1863°. This is the so-called "Molecular depression of freezing point". For 1 mole dissolved in 1 liter of water, the lowering of freezing point is evidently 1·863° C. This agrees excellently with that found by Raoult. Note, however, that Raoult's definition of molecular lowering refers to 1 mole dissolved in 1 *gram* of solvent, and similarly for the molecular rise of boiling point.

The Fifth Method, depending on the rise of boiling point, is identical in principal with the preceding. Take as an illustration the case of water as solvent—

L = latent heat of vaporisation per gram = 540 calories;
ρ = 1 (approx.);
R = 1·985;
T_2 = 373°;

$$\therefore \frac{RT_2^2}{L\rho} = 514·8°.$$

Hence for 1 mole dissolved in 1 c.c. "the molecular elevation of the boiling point of water" is 514·8°. For 1 mole dissolved in 1 liter of water the rise of boiling point is 0·5148°. It should be pointed out that the expressions for "molecular depression of freezing point" and "molecular elevation of boiling point" are never realised in practice, *i.e.* they have theoretical significance only. The solubility of substances would not allow of 1 mole of substance being dissolved in 1 c.c., and even if this could be obtained, the solution would be so extremely concentrated that the solute would certainly not obey the gas law, and hence it would not be justifiable to write P = RTC.

As regards the experimental details of the usual methods of determining the molecular weights of dissolved substances by the lowering of freezing point or the rise of boiling point, reference may be made to any textbook of practical physical chemistry. Attention may also be drawn to two more unusual methods of carrying out the boiling point determination. The first of these is the dew-point method originated by Cumming (*Trans. Chem. Soc.*, **95**, 1772, 1909) and modified by McBain. This method is described in Chap. XI. in connection with McBain's determination of the molecular weights of solutes in soap solutions. The second method is that introduced by Cottrell (*Journ. Amer. Chem. Soc.*, **41**, 721, 1919) and tested thoroughly by Washburn (*ib.*, p. 729). The principle of Cottrell's method is as follows:—

Whereas the determination of the boiling point of a *pure* liquid is an exact and fairly simple operation, the determination of the boiling point of a solution as ordinarily carried out is inexact. The fundamental difficulty lies in the fact that whilst it is possible in the case of the pure substance to place the thermometer in the vapour and not in the liquid itself and to allow recondensation to give it a thin coating of liquid in temperature equilibrium with the vapour, such procedure is not followed in the case of solutions in the ordinary apparatus; instead we have to insert the thermometer in the liquid solution itself, because of course the *vapour* over the solution is at a slightly lower temperature than the liquid. By inserting the thermometer in the liquid, however, we expose it to the variable superheating effects which always occur in heated liquids. The essence of Cottrell's method is to remove the thermometer from the body of the liquid solution and to place it above the solution, at the same time causing a thin stream of liquid solution to pass over the bulb of the thermometer by artificial means, thereby simulating the conditions which are known to give satisfactory results in the case of a pure liquid. Some of the liquid solution is driven by its own boiling up a narrow tube having an opening in the side through which the liquid is ejected and trickles back over the thermometer, the temperature of which is read in the ordinary way.

Referring to the usual method of determining the boiling point of a solution by immersion of the thermometer in the liquid, Cottrell draws attention to the fact that even if no superheating occurred the boiling point (of the solvents usually employed) at a depth of 3 or 4 cms. below the surface would still be approximately 0·1° higher than

at the surface owing to the pressure of this column of liquid; consequently no matter how thoroughly the equilibrium between vapour and liquid may be attained the thermometer actually measures a roughly averaged temperature throughout the liquid.

A Sixth Method of determining molecular weight, namely, that depending upon variation of the solubility of the solute with temperature, will be referred to later.

Determination of Electrolytic Dissociation and Degree of Hydrolysis by Measurements of Freezing Point and Boiling Point.

Since the methods for determination of molecular weights give in the first place the *number* of individuals present in a solution, it is clear that the electrolytic dissociation of an electrolyte in water will be made evident by abnormal lowering of freezing point and rise of boiling point owing to the extra number of new individuals, ions, produced. In fact, a binary electrolyte whose degree of dissociation at the given dilution is α will produce the abnormal effect indicated, the magnitude of which is $\frac{1+\alpha}{1}$. Similarly, hydrolysis, since it produces new individuals in solution, will likewise cause a further abnormal lowering of freezing point and rise of boiling point. Determinations of electrolytic dissociation by these methods have been made by Jahn and Abegg. Reference may be made to a recent investigation by W. A. Roth (*Zeitsch. für physik. Chem.*, **79**, 610, 1912) on the dissociation of some strong electrolytes, caesium nitrate, potassium nitrate, sodium nitrate, and silver nitrate in water, by the lowering of freezing point method. He found that the Ostwald's Dilution Law was *not* obeyed by these salts (*cf. Washburn*, Chap. V. (Vol. I.)). In general, however, these methods are not suitable for this type of measurement (unless extreme precautions are taken), the most generally applicable methods being those already given in Vol. I., and the electro-metric method, which will be given later.

Illustrations.—Problem 72, in Knox's *Physico-Chemical Calculations:* The freezing point of a solution of $a = 0{\cdot}684$ gram of cane sugar in 100 grams of water is $t_1 = -0{\cdot}037°$ C.; and that of a solution of $b = 0{\cdot}585$ gram of sodium chloride in 100 grams of water is $t_2 = -0{\cdot}342°$ C. What is the apparent molecular weight of the salt at this concentration, and what is its per cent. dissociation?

According to Raoult's Law (just proved)—

$-\Delta T = kC$ when C is expressed in moles;

if M = molecular weight of sugar in solution,

and M_1 = molecular weight of sodium chloride in solution,

then in the first case the molecular concentration per liter is $\frac{a10}{M}$, and in the second case $\frac{b10}{M_1}$.

Hence by Raoult's Law—

$$\frac{a10}{M} : \frac{b10}{M_1} = \Delta T_1 : \Delta T_2.$$

$$\therefore M_1 = \frac{342 \times 0{\cdot}585 \times 0{\cdot}037}{0{\cdot}342 \times 0{\cdot}684} = 31{\cdot}65$$

where 342 is the molecular weight of dissolved sugar.

Now if the fraction dissociated per mole of sodium chloride is α, then there are $(1 - \alpha)$ undissolved moles and 2α dissolved ions. Hence total number of individuals in solution is $(1 + \alpha)$. If there had been no dissociation there would be only one individual in solution, and its molecular weight would have been $23 + 35{\cdot}5 = 58{\cdot}5$. Now when a given mass in grams is dissolved, its weight is evidently equal to the number of individuals × weight of each individual. The weight of each individual is the apparent weight = 31·65. Hence the mass of salt in grams = $(1 + \alpha)$ 31·65.

If no dissociation had occurred the same mass of salt in grams would = 1 × 58·5.

$$\therefore 58{\cdot}5 = 31{\cdot}65(1 + \alpha)$$

$$\therefore \alpha = 0{\cdot}85$$

or $\alpha = 85$ per cent.

Problem 74, Knox's *Physico-Chemical Calculations:* Ether boils at 35° C. under 760 mm. pressure. On dissolving 12·8 grams naphthalene (M = 128) in 100 grams of ether the rise in boiling point is 2·1°. What is the latent heat of vaporisation of ether?

The molecular weight of naphthalene is 128. Hence the solution is $\frac{12{\cdot}8 \times 10}{128} = 1$ molar weight normal, or $\frac{1}{1000}$th of a mole in 1 gram of ether, *i.e.* 1 gram-mole per 1000 grams of ether $= \frac{C}{\rho} = \frac{1}{1000}$.

Van 't Hoff's expression gives—

$$L = \frac{RT^2C}{\Delta T\rho}$$

$$= \frac{2 \times (273 + 35)^2 \times 1}{2{\cdot}1 \times 1000} = 89{\cdot}7 \left\{ \begin{matrix} \text{calories per gram} \\ \text{of solvent.} \end{matrix} \right.$$

It must be remembered that the solutes considered in the five methods are *non*-volatile.

The Variation of the Equilibrium Constant in Dilute Solution with Temperature.

As we have already shown that the osmotic pressure of dissolved substances in dilute solution obeys the gas laws, one can infer that the thermodynamic deduction, already given, of the mass law for the gaseous state can at once be transferred to the state of solution. An analogous cycle could be carried out with two "equilibrium boxes" immersed in a reservoir of solvent of infinite size; a series of semi-permeable pistons

being required for the transfer of the various substances from one box to the other. Naturally, when the solution is of such a concentration that the gas expression P = RTC no longer holds, the work expression $RT \log \frac{c_1}{c_2}$ will also be inapplicable, just as the analogous expression, $RT \log \frac{p_1}{p_2}$ for the gaseous state is likewise inapplicable, if the gases do not obey the simple law.

Having found in this manner the thermodynamic justification of the law of mass action for dissolved substances, we can apply the van 't Hoff isochore, *viz.*—

$$\frac{\partial \log K}{\partial T} = \frac{Q_v}{RT^2},$$

where K is the equilibrium constant, and Q_v the heat of the reaction taking place in the solution.

As an illustration of the use of the isochore in solution, we may now proceed with the Sixth Method of determining molecular weight. Consider a substance not too soluble in a solvent, *i.e.* one for which a solution of maximum concentration, *i.e.* its solubility, obeys the gas laws. Suppose that at a given temperature T_1 the solubility is s_1, and at another temperature T_2 the solubility is s_2. In each case there is equilibrium between the solid phase and the saturated solution. If the "reaction," *i.e.* the process of solution, simply involves the transfer of 1 mole from the one phase to the other, we can regard the equilibrium finally reached as conditioned by an expression of the form $\frac{s_1}{C} = K_1$, where K is a mass law constant. C is the concentration of the solid in the solid phase, *i.e.* in itself, and may therefore be regarded as unity. Hence at a given temperature T_1 we have $s_1 = K_1$. At another temperature T_2 we have $s_2 = K_2$. Hence instead of the term $\frac{\partial \log K}{\partial T}$ we can write $\frac{\partial \log s}{\partial T}$, and substitute this in the isochore, *viz.*—

$$\frac{\partial \log s}{\partial T} = \frac{Q_v}{RT^2}, \text{ or } \frac{1}{s}\frac{\partial s}{\partial t} = \frac{Q_v}{RT^2}.$$

Integrating between the two temperatures T_1 and T_2 with the approximate assumption that Q_v is a constant, we obtain—

$$\log s_2 - \log s_1 = \frac{Q_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

If the molecular weight of the dissolved substance is M, and x_1 grams are dissolved in V c.c. at T_1, then $s_1 = \frac{x_1}{MV}$, and at T_2, $s_2 = \frac{x_2}{MV}$. By measuring the heat of solution of, say, 1 gram, and measuring the solubility in grams per cubic centimeter at the two temperatures, we can obtain M. Van 't Hoff, in his lectures (Vol. II., p. 59) quotes the following: 100 parts of water dissolve 2·88 and 4·22 grams of succinic

acid at 0° and 8·5° respectively. Using the differential equation as it stands, and putting $\frac{\partial s}{\partial t}$ as small finite changes Δs and Δt, we get—

$$Q = \frac{RT^2}{s} \frac{\Delta s}{\Delta T} = 6830 \text{ calories per mole.}$$

The observed heat of solution per gram is 55, and therefore the molecular weight $= \frac{6830}{55} = 124$, calculated $= 118$.

The Variation with Pressure of the Equilibrium Constant of a Reaction in Dilute Solution.

The equilibrium constant here referred to is that defined either in volume concentration terms (gram-molecules per liter) or in terms of partial pressures. It has already been shown in the case of a *gaseous* system that the equilibrium constant defined in either of these two ways is independent of external pressure. We are not considering at the moment the third way of defining the equilibrium constant (Planck's form), in which molecular concentrations or molar fractions are employed. The latter equilibrium constant, which we have already discussed in the case of gases, varies with the external pressure even in the gaseous case, and, as Planck has shown, varies likewise in the case of a reaction in solution. We are concerned at present, however, with the ordinary equilibrium constant K defined in terms of volume concentrations. The considerations apply equally well to the constant defined in terms of partial osmotic pressures.

The equilibrium constant K in the case of solutions can vary with the total pressure exerted upon the solution, by means of a piston or by an inert gas. This behaviour is in contrast with the behaviour of gaseous systems. The distinction is due to the fact that in gaseous systems the total pressure exerted upon the system is necessarily equal to the sum of the partial pressures of the constituents, whilst in solutions the external pressure is by no means identical with the total osmotic pressure (due to the sum of the partial osmotic pressures of the solutes), a very large increase in external pressure having as a rule a relatively small effect upon the volume of the solution, and therefore a very small effect upon the osmotic pressure. In short, whilst the equilibrium constant K (expressed in moles per liter) is independent of the total *osmotic* pressure of the constituents of the system, it is not necessarily independent of the external pressure applied to the solution. The effect of this external pressure upon the value of K has been investigated by J. Rice (Trans. Faraday Soc., **12**, 318 (1917)), by means of a thermodynamical cycle. In the paper referred to, Rice obtained an expression for the variation of K, as defined above, which he showed was not in agreement with that obtained by Planck for the corresponding variation of K_{Planck}. The source of the discrepancy was later pointed out by A. M. Williams (*Trans. Faraday Soc.* (1920)). The following is the corrected cycle given by Rice:—

Consider three substances (A, B, C) which when dissolved in a definite solvent are connected by the reaction—

$$\lambda \text{ mols of A} \rightleftarrows \mu \text{ mols of B} + \nu \text{ mols of C.}$$

(The restriction to three substances is merely a matter of convenience in exposition; it involves no loss of generality in the reasoning.)

Let there be a large quantity of the solvent, on the surface of which is exerted a pressure P.

In this mass of solvent let us have three large reservoirs containing respectively—

l mols of A at the concentration a mols per liter;
m „ B „ „ b „ „
n „ C „ „ c „ „

The sides of the reservoirs are permeable to the solvent, but not the dissolved substances.

Let us also have an equilibrium box containing a mass of the three substances in solution at the equilibrium concentrations α, β, γ mols per liter respectively. The box sides are also permeable to the solvent but not to A, B, and C.

By means of pistons, cylinders, and semipermeable membranes take λ mols of A from its reservoir and convert them into μ mols of B and ν mols of C in their respective reservoirs, *via* the box. In doing this, however, we have to remember that the pressure exerted upon the solvent inside any one of the reservoirs is greater than the pressure P upon the solvent surrounding the reservoirs by an amount equal to the osmotic pressure p due to the solute in any one of the reservoirs. When we remove solute, we likewise remove a certain amount of solvent with it, and since the solvent is not incompressible, it will expand slightly on being withdrawn from a reservoir. Similarly on adding, say, a grammole of solute to a reservoir, the accompanying solvent is compressed and decreases in volume. These changes in volume of the solvent at different stages in the cycle have to be allowed for in the work terms, in addition to the ordinary osmotic work terms associated with the transference of solute, *i.e.* associated with the thermodynamic method of carrying out the purely chemical reaction itself. With this hint as to the attention which has to be paid to the behaviour of the solvent, we may now take up the various stages of the cycle systematically.

In order to maintain the concentrations in the reservoirs at a, b, and c respectively, we must decrease the volume of the first reservoir so as to expel from it λ/a liters of solvent and increase the volumes of the remaining two reservoirs so as to admit to them μ/b and ν/c liters of solvent respectively.

Any change of volume which has taken place in the *whole system* owing to these occurrences is the sum of two parts: (1) That due purely to the chemical reaction. Thus in withdrawing one mole of A from the solution of A in the first reservoir we decrease the volume of the first reservoir by a definite amount V_A, where V_A is the molar volume of A, *i.e.* the space occupied by the mole of solute A considered apart

from the solvent. Hence in withdrawing λ moles we decrease the volume by λv_A, the solution being assumed to be dilute. Similarly, we increase the volumes of the other reservoirs by μv_B and νv_C, giving an increase in the *whole system* due to this of

$$(\mu v_B + \nu v_C - \lambda v_A) \text{ liters.}$$

(2) In addition to (1) we have to consider any change in volume of the whole system produced by the expulsion of solvent from a reservoir or admission of it to a reservoir. This would involve no change if the solvent were under the same hydrostatic pressure inside a reservoir as in the general mass outside. But this is not so. Outside, the pressure on the solvent is P; inside the first reservoir it is under the pressure P plus the osmotic pressure p_A of the solute which we maintain constant by the device of expulsion of λ/a moles of solvent when withdrawing λ moles of the solute. Hence, if ϵ is the compressibility of the solvent, the λ/a moles of solvent in escaping from a place where the pressure is $P + p_A$ to a place where the pressure is P, will increase in volume by $p_A . \epsilon . \lambda/a$, *i.e.* by $RT . \lambda . \epsilon$ since $p_A/a = RT$. Similarly, in admitting μ/b and ν/c moles of solvent to the other reservoirs there will be a decrease in volume of $RT(\mu + \nu)\epsilon$. Hence, if we are to keep the concentrations in the reservoirs unchanged we must in addition to (1) have a change of the volume of the whole system, which is a *decrease* of amount

$$RT(\mu + \nu - \lambda)\epsilon.$$

In consequence, therefore, not only of the reaction but also of the preservation of the concentrations in the reservoirs we can say that—

$$V_2 - V_1 = \mu v_B + \nu v_C - \lambda v_A - RT(\mu + \nu - \lambda)\epsilon \quad . \quad (1)$$

where V_1 is the volume of the *whole system* at the beginning of the reaction and V_2 is the total volume at the end.

During the reaction occurring at constant external pressure P on the system as a whole the external work will be the sum of two terms. (*a*) The work of the osmotic pressures during the passage of the substances from the reservoirs into and out of the box, *viz.*—

$$RT \log K - RT \log (b^\mu c^\nu / a^\lambda). \quad . \quad . \quad (2)$$

[In order that this expression may be correct we must maintain the concentrations in the reservoirs unchanged. Hence arises the necessity of expelling and admitting solvent as indicated above.]

(*b*) As there is an increase in volume, $V_2 - V_1$ of the whole system against a constant external pressure P, there will be in addition to (*a*) work done by the system of amount

$$P(V_2 - V_1) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Up to this point we have been dealing with the first step of the cycle.

In the second step we *gradually* change the pressure on the solvent surface from P to P′ and gradually change the volume of the system from V_2 to V'_2. This will not involve a change in the concentrations

a, b, c; for although more solvent will be compressed into the reservoirs through the sides, yet the masses $l - \lambda$, $m + \mu$, $n + \nu$ will remain unchanged, and so *volume* concentrations will not alter. It may be otherwise for the box; for though compression of more solvent into the box will not alter the total mass of the dissolved substances inside it, yet it may affect the partial masses of each substance and vary the equilibrium concentrations to α', β', γ', and the constant to K'.

In this step the work of the system is—

$$\int_{V_2}^{V'_2} p dv_2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where p is any value of the pressure between the values P and P', and v_2 the corresponding total volume of the $l - \lambda$ mols of A, $m + \mu$ mols of B, $n + \nu$ mols of C, the solution in the box, and the mass of solvent outside reservoirs and box, all at pressure p.

In the third step, while maintaining the pressure at P', we transform μ mols of B and ν mols of C into λ mols of A, *via* the box. This will involve a change of volume from V'_2 to V'_1, and the system will do work which is the sum of two terms, as in the first step, *viz.*—

$$RT \log (1/K') - RT \log (a^\lambda / b^\mu c^\nu) + P'(V'_1 - V'_2)$$

or

$$RT \log (b^\mu c^\nu / a^\lambda) - RT \log K' - P'(V'_2 - V'_1) \quad . \quad . \quad (5)$$

In the fourth step we gradually change the pressure back to P and the volume back to V_1; the work of the system during this change is—

$$\int_{V'_1}^{V_1} p dv_1 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where, as before, p is a pressure between P and P', and v_1 is the total volume of solvent, l mols of A, m mols of B, n mols of C, and a mass of solution at equilibrium concentrations corresponding to the pressure p. [It is necessary to note that v_1 is not equal to v_2; *i.e.* it is not the same function of p as v_2; thus when $p = P$, $v_1 = V_1$ and $v_2 = V_2$; and when $p = P'$, $v_1 = V'_1$, and $v_2 = V'_2$.]

Summing up the various work terms given in (2) to (6), the result must be zero. Hence—

$$\begin{aligned} &RT(\log K - \log K') \\ &+ P(V_2 - V_1) - P'(V'_2 - V'_1) \\ &+ \int_{V_2}^{V'_2} p dv_2 - \int_{V_1}^{V'_1} p dv_1 \\ &= 0. \end{aligned}$$

By a partial integration—

$$\int_{V_1}^{V'_1} p dv_1 = P'V'_1 - PV_1 - \int_{P_1}^{P'} v_1 dp$$

and

$$\int_{V_2}^{V'_2} p dv_2 = P'V'_2 - PV_2 - \int_{P}^{P'} v_2 dp.$$

Hence the above equation becomes, after cancellation of certain terms—

$$RT(\log K - \log K') = \int_P^{P'} (v_2 - v_1)dp = \int_{P'}^{P} (v_1 - v_2)dp \quad . \quad (7)$$

Had we carried out the operations described between the pressures $P + \delta P$ and P', we should have had

$$RT[\log(K + \delta K) - \log K'] =$$

$$\int_{P'}^{P+\delta P} (v_1 - v_2)dp = \int_{P'}^{P} (v_1 - v_2)dp + (V_1 - V_2) \cdot \delta P \quad . \quad (8)$$

where $K + \delta K$ is the constant for pressure $P + \delta P$. Therefore subtracting (7) from (8) we have—

$$RT[\log(K + \delta K) - \log K] = (V_1 - V_2)\delta P,$$

or proceeding to the limit—

$$\frac{d \log K}{dP} = \frac{V_1 - V_2}{RT} \quad . \quad . \quad . \quad (9)$$

This is the expression required.

This result is sometimes stated in terms of an equilibrium constant defined by means of concentrations which are pure ratios, *viz.* the quotient of the number of moles of a dissolved substance by the total number of moles present, *solvent moles included.* This is the constant used by Planck (*Thermodynamics*, *English Trans.*, Chap. V.). In deducing equation (9) above, the K is expressed in concentration terms which are moles per liter. We have denoted the latter concentrations by α, β, λ above. Let us denote concentrations in Planck's sense by x, y, z; let us also denote Planck's K by K_{Planck} or $K_{Pl.}$

Then $K = \beta^\mu \gamma^\nu / \alpha^\lambda$

and $K_{Pl.} = y^\mu z^\nu / x^\lambda$.

If there are n_0 moles of solvent, and n_1 moles of A, n_2 moles of B, and n_3 moles of C in the equilibrium box, which has a volume V (say), then—

$$x = \frac{n_1}{n_0 + n_1 + n_2 + n_3} = \frac{n_1}{N}$$

$$y = \frac{n_2}{N}, \quad z = \frac{n_3}{N},$$

while

$$\alpha = \frac{n_1}{V}, \beta = \frac{n_2}{V}, \gamma = \frac{n_3}{V}.$$

$$\therefore K = K_{Pl.}(N/V)^{\mu+\nu-\lambda}.$$

Hence $$\log K = \log K_{Pl.} - (\mu + \nu - \lambda) \log v,$$

where $$v = V/N$$

and $$\therefore \frac{d \log K}{dP} = \frac{d \log K_{Pl}}{dP} - (\mu + \nu - \lambda) \frac{1}{v} \frac{dv}{dP}.$$

Or $$\frac{d \log K}{dP} = \frac{d \log K_{Pl.}}{dP} + (\mu + \nu - \lambda)\epsilon,$$

since the compressibility $\epsilon = -\frac{1}{v}\frac{dv}{dP}$.

Hence $$\frac{d \log K_{Pl.}}{dP} = \frac{V_1 - V_2}{RT} - (\mu + \nu - \lambda)\epsilon.$$

But by equation (1)—

$$V_2 - V_1 = \mu v_B + \nu v_C - \lambda v_A - RT(\mu + \nu - \lambda)\epsilon.$$

Hence $$\frac{d \log K_{Pl.}}{dP} = \frac{\lambda v_A - \mu v_B - \nu v_C}{RT}$$

$$= \frac{\text{diminution in volume due to reaction alone}}{RT}.$$

The expression which we wish to test experimentally is—

$$\frac{d \log K}{dP} = \frac{V_1 - V_2}{RT}.$$

This may be illustrated by some experiments of Fanjung (*Zeitsch. physik Chem.*, **14**, 673, 1894), who by means of conductivity measurements determined the dissociation constants (the Ostwald constant) for a series of weak acids in aqueous solutions at various pressures. It appears to be a general conclusion that the process of ionisation is accompanied by a contraction, or decrease in volume. Hence the Le Chatelier-Braun principle (embodied quantitatively in the above expression) predicts that on increasing the pressure the degree of dissociation should *increase* also, that is the dissociation constant should increase. Fanjung found this to be the case. The term $V_1 - V_2$ in this case represents the contraction due to the transfer of 1 gram-mole from the unionised to the ionised state. For acetic acid at 18° C. Fanjung found that

$$\log_{10} K_1 = \bar{5}\cdot 254$$

at 1 atmosphere pressure, and at 260 atmospheres

$$\log_{10} K_2 = \bar{5}\cdot 305.$$

Using the differential equation as it stands—

$$\left(\frac{\partial \log_e K}{\partial p}\right)_T$$

may be written $$2\cdot 302\left(\frac{\log_{10} K_2 - \log_{10} K_1}{259}\right)$$

so that the contraction per mole

$$= \frac{-\ 0\cdot 0821 \times 291 \times 2\cdot 302(0\cdot 305 - 0\cdot 254)}{259}$$

$$= -\ 0\cdot 0108.$$

Since the pressure has been expressed in atmospheres and R in liter-atmospheres (0·0821), the contraction is expressed in liters. Hence the contraction in c.c. per mole is 10·8 c.c. In the following table Fanjung's calculated values for various acids are compared with values observed by Ostwald (from measurements of the volume change on neutralisation of the acid with a strong base).

Acid.	Contraction Observed.	Contraction Calculated.
	c.c.	c.c.
Formic	7·7	8·7
Acetic	10·5	10·8
Propionic	12·2	12·4
Butyric	13·1	13·4
Iso-butyric	13·8	13·3
Lactic	11·8	12·1
Succinic	11·8	11·2
Maleic	11·4	10·3

The agreement is satisfactory.

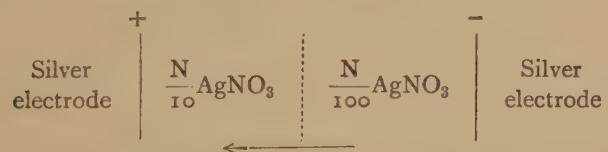
CHAPTER VII.

Chemical equilibrium in homogeneous systems—Dilute solutions (*continued*)—Outlines of the electrochemistry of dilute solutions.

Electrochemistry of Dilute Solutions.[1]

Nernst's Theory of the "Solution Pressure" of an Electrode.

If an electrode of silver be placed in a solution of silver nitrate there will be an electrical potential difference (represented by P.D.) between the electrode and the solution. When an electrode is in contact with a solution containing ions of the same metal as the electrode itself, the electrode is said to be reversible. A cell fitted with a reversible electrode is said to be a reversible cell. The simplest type of reversible cell is that denoted by the term "concentration cell". An example of this may be represented by the arrangement—



Such a combination yields quite an appreciable e.m.f., the electrode in contact with the decinormal solution being in this case the positive pole, *i.e.* current flows *inside* the cell from right to left. The nett e.m.f. of this cell depends on the three single P.D.'s, namely, the P.D., $Ag \mid AgNO_3\frac{N}{10}$; P.D., $AgNO_3\frac{N}{10} \mid AgNO_3\frac{N}{100}$; and P.D., $Ag \mid AgNO_3\frac{N}{100}$.

The P.D. where the liquids meet (known as the liquid | liquid P.D. or contact P.D.) is in such a case very small compared with either of the P.D.'s at the electrodes. The mechanism of the production of these

[1] In a short chapter in a book of this nature it is quite futile to attempt any comprehensive discussion of electromotive force. Only the fundamental notions can be indicated. The student is therefore referred to the textbooks dealing specifically with Electrochemistry, especially Le Blanc's *Electrochemistry* (English or German edition), Lehfeldt's *Electrochemistry* (in this series of textbooks), and the recent work by Allmand, *Applied Electrochemistry*. This latter book is of special significance in showing the *scientific* application of pure electrochemistry to industrial problems. As regards laboratory experimental methods, *i e.* the measurement of e.m.f., details may be found in any of the textbooks on practical physical chemistry

potential differences has been explained in an extremely clear manner by Nernst, and as they are essentially dependent upon the osmotic pressure of the ions, it is only proper to consider them in dealing with dilute solutions from the thermodynamic standpoint. Consider the case of a metal like silver in contact with an aqueous solution of silver nitrate, *i.e.* Ag^+ ions. According to Nernst (*Zeit. physik. Chem.*, **2**, 613; **4**, 129, 1889), all metals possess a property which he calls solution pressure or solution tension. In virtue of this property the metal tends to drive ions (positively charged) from itself into the surrounding solution. If the solution happen to contain these ions already (say silver ions in the case considered), then in virtue of their osmotic pressure, they will tend to drive themselves on to the surface of the metal. The osmotic pressure of the ions in solution opposes therefore the solution pressure of the metal itself. If these two effects just balance, there will be no transfer of ions at all, that is no transfer of electricity, and consequently there will be no P.D. between the electrode and the solution. But this would only be an exceptional and particular case. In general the two effects do not neutralise one another. In the case of zinc, for example, in contact with a zinc salt solution, the solution pressure of this metal is so great that Zn^{++} ions always leave the electrode and pass into the solution. This process would appear at first sight to be capable of going on *ad infinitum*, but as a matter of fact only an exceedingly small mass of the metal is thus transferred (a quite unweighable amount), for as the positive ions pass from the metal into the solution, they leave the metal negatively charged, and this makes the further expulsion of positive ions more difficult owing to the electrostatic attraction of the negatively charged metal for the positively charged ions. An equilibrium state is thus instantaneously reached when the solution pressure of the zinc is just balanced by the osmotic pressure of the ions originally present in the solution, and by the electrostatic field set up between the metal and the layer of positive ions driven out by the metal. In such a case there is a P.D. between the metal and the layer of ions, that is, we say that there is a P.D. at the electrode, and since the metal, in this case zinc, is negatively charged compared to the layer, we say that the zinc electrode is negative compared to the solution. In the case of silver the solution pressure has been shown (cf. later) to be so small that the osmotic pressure of the silver ions (say of a $\frac{N}{10}AgNO_3$ solution) easily overcomes it, and deposits positive ions on the electrode, an electrostatic field being set up between the metal and the solution, but in this case the electrode is positively charged with respect to the solution, *i.e.* there is a *a fall* of potential in going from the electrode to the solution. Suppose that, in the case of silver dipping into a solution of silver nitrate, the steady state is reached (this is done instantaneously),[1] the P.D. being π (volts),

[1] In the case of silver nitrate (cited) it is true that the steady P.D. characteristic of the electrode is reached practically instantaneously. In many other cases, however, some time must be allowed for the steady value to be attained. According

the solution pressure of the metal being denoted by P, and the osmotic pressure of the solution by p, *i.e.* the osmotic pressure of the positive ions in the solution. Then we can imagine a small virtual change in the system, namely, the transfer of δx gram ions of the metal (carrying a quantity of electricity δF faradays) from the electrode to the solution. Since the system is in equilibrium the work at constant volume is zero. The electrical work is obviously $\pi\delta$F. There is likewise work analogous to a three-stage distillation or osmotic work term, also involved in bringing the δx gram ions from the solution pressure P to the osmotic pressure p. This work by analogy is—

$$\delta x \mathrm{RT} \log \frac{\mathrm{P}}{p}.$$

By the principle of virtual work we can write—

$$\pi\delta\mathrm{F} + \delta x \mathrm{RT} \log_e \frac{\mathrm{P}}{p} = 0,$$

or

$$\pi\delta\mathrm{F} = -\delta x \mathrm{RT} \log_e \frac{\mathrm{P}}{p}$$

but $\frac{\delta\mathrm{F}}{\delta x}$ = quantity of electricity associated with 1 gram ion of the metal = nF, when n is the valency of the ion (the number of positive charges carried), and F is the faraday, *i.e.* 96,500 coulombs. Hence we can write—

$$\pi = -\frac{\mathrm{RT}}{n\mathrm{F}} \log_e \frac{\mathrm{P}}{p} = -\frac{2{\cdot}303\mathrm{RT}}{n\mathrm{F}} \log_{10} \frac{\mathrm{P}}{p}.$$

$$\therefore \pi = \frac{2{\cdot}303\ \mathrm{RT}}{n\mathrm{F}} \log_{10} \frac{p}{\mathrm{P}}$$

where 2·303 is the factor for the reduction of $\log_e$ to $\log_{10}$.

Note on Virtual Work.—It is essential to be clear as to the *sign* of each virtual work term in the correct application of the principle. It is therefore necessary to be able to visualise as far as possible the mechanism of the process. A work term must be reckoned as essentially *positive* if the force (which does the work) *assists* the motion of the mass moved, or is in the same direction as the motion. When

---

to Newbery a strip of sheet copper cleaned and cut into two pieces will give, when these pieces are connected to a micro-ammeter and immersed in $CuSO_4$ solution, a gradually decreasing current for two or three days. This procedure of short-circuiting the two (apparently identical) electrodes is always resorted to before setting up a concentration cell (q.v.) in order that the metals may be as far as possible in the same state. Some process occurs in the surface layer which may possibly be a kind of surface crystallisation of the metal or orientation of the atoms in the surface as a result of slight electrolysis. In the case of the calomel electrode (referred to later in the text) at least ten minutes must elapse before the electrode "settles down" to its final value. The mechanism of such time effects at electrodes is obscure in spite of the considerable amount of investigation carried out upon the allied problems of "passivity" and "overvoltage" of different metals.

[1] For another method of reducing this relation, see Nernst's *Theoretical Chemistry*, English translation of the 6th German edition, p. 757.

the force *opposes* the motion which the mass or particle is conceived of as undergoing the work term is negative. The same statement regarding sign may be restated thus: the work term is to be reckoned as *positive* if the force and motion make an *acute* angle with one another, *negative* if they make an obtuse angle. Thus taking the case of a silver electrode in silver nitrate solution, consider the motion of δF units of *positive* electricity from electrode to solution. Since the solution is known to be negatively charged compared to the electrode, the electric force assists the motion of the *positive* charge, and therefore if π be the potential difference $\pi\delta F$ is a positive term. [Had the electricity been negative, it would have been necessary to write: $-\pi\delta F$.] Further, the solution pressure assists the motion of the particle in the direction considered. Its effect is therefore *positive*. The osmotic pressure of the Ag ions opposes the motion, and the resulting work term is therefore to be given a *minus* sign. If these two forces appear in one work expression (a logarithmic expression), the term P must be in the numerator, p in the denominator. All the work terms are then algebraically added and equated to zero, *i.e.* in the above case—

$$\pi\delta F + \delta x \, RT \log \frac{P}{p} = 0.$$

To obtain π in volts it is necessary that $\frac{RT}{nF}$ should likewise be expressed in terms of the same units (*i.e.* the unity of energy must be the volt-coulomb or joule). The numerical value for R must be therefore 8·32. For a temperature of 18° C. the expression—

$$\frac{2{\cdot}303RT}{nF} = \frac{0{\cdot}058}{n}$$

so that $$\pi \text{ volts } 18^\circ \text{ C.} = \frac{0{\cdot}058}{n} \log_{10} \frac{P}{p}$$

at 25° C. $$\pi \text{ volts } 25^\circ \text{ C.} = \frac{0{\cdot}059}{n} \log_{10} \frac{P}{p}.$$

For silver and other monovalent metals n is unity. Instead of using the pressure terms P and p, one may also substitute concentration terms C and c respectively (where c denotes throughout the concentration of metallic ions), and write—

$$\pi = -\frac{RT}{nF} \log_e \frac{C}{c} \text{ or } \frac{RT}{nF} \log \frac{c}{C} \text{ or } \frac{RT}{nF} \log c + \text{constant}.$$

The quantity denoted by C bears the same relation to the solution pressure P as c (the concentration of the metallic ions in solution) bears to p (the osmotic pressure of the ions in solution). It is difficult, indeed impossible, to ascribe any real *physical* significance to the quantity C, owing to the difficulty of ascribing a really definite physical significance to P itself. Naturally a theoretical expression of this nature has been subjected to a considerable amount of criticism. Thus Lehfeldt (*Phil. Mag.*, [V], **48**. 430, 1899) has laid stress on the fact that if the numerical values for P are calculated for metals (as of course can be done, at least approximately, from measurements of the e.m.f. at the electrode—for an account of the method of measuring single PD.'s, reference should be made to some textbook of *Electrochemistry*), it is found that these numerical values vary from the infinitely great to the infinitely small. Thus—

P for zinc = $9{\cdot}9 \times 10^{18}$ atmospheres
„ nickel = $1{\cdot}3 \times 10^{0}$ „
„ palladium = $1{\cdot}5 \times 10^{-36}$ „

Lehfeldt says: "There are certain obvious difficulties in the way of accepting these numbers as representing a physical reality. The first of them is startlingly large; that, however, may not be a true difficulty. The third is so small as to involve the rejection of the entire molecular theory of fluids. If it is true that fluids consist of molecules with a diameter of the order of magnitude of 10^{-8} cm., then the production of a pressure so low is impossible; for pressure is a statistical effect due to the impact of numerous molecules. Krüger (*Zeit. physik. Chem.*, **35**, 18, 1900) replies to Lehfeldt's criticism, pointing out that the P or C term is really an integration constant (this, however, does not get us any nearer the point regarding the physical significance of P or C, if indeed there is any physical significance to be attached at all). In this connection reference should also be made to an earlier paper by Luther (*Zeit. physik. Chem.*, **19**, 1896). For a further discussion of this point, the reader must consult a textbook of Electrochemistry. It may only be pointed out here, that the vagueness respecting the term P involves a corresponding vagueness regarding the "three-stage thermodynamic distillation process," the work of which we have denoted by $RT \log \frac{P_1}{p}$.

The general conclusion which has been come to, however, is that the Nernst method of treatment of e.m.f. in cells represents a great advance in our knowledge of this important phenomenon. One or two simple cases of the application of the osmotic theory will now be given.

Concentration Cells ("*Concentration Cells with Transport*").

A concentration cell consists essentially of two similar electrodes dipping into solutions of the same salt, the solutions being at different concentrations of the salt, c_1 and c_2,[2] at the two electrodes, both solutions being either in direct contact or separated by a conducting substance of some kind. The source of e.m.f. is to be found in the tendency of the two solutions to equalise their concentrations. The apparatus used is represented in diagrammatic form (Fig. 23) for the case of silver electrodes in a water solution of silver nitrate. This can be more conveniently expressed as—

$$\begin{array}{c|c|c|c} \text{Ag} & \begin{array}{c}\text{AgNO}_3\\ c_1\end{array} & \begin{array}{c}\text{AgNO}_3\\ c_2\end{array} & \text{Ag} \\ \multicolumn{1}{c}{} & \multicolumn{1}{c}{} & \multicolumn{1}{c}{} & \multicolumn{1}{c}{} \\ \multicolumn{1}{c}{e_1} & \multicolumn{2}{c}{} & \multicolumn{1}{c}{e_2} \end{array}$$

This particular type of cell is known as a concentration cell of the First

[1] An attempt to visualise what is meant by solution pressure has recently been made by Smits, *Proc. K. Akad. Wetensch.*, Amsterdam, **18**, 1485 (1916).

[2] More strictly, c_1 and c_2 refer to concentration of the same *ion*.

Type. We may neglect the liquid | liquid P.D. between the solutions. This can be accomplished in practice by the interposition of saturated ammonium nitrate solution or saturated KCl at the junction of the two liquids. This is supposed to have the property of nullifying liquid potential differences. By means of the NH_4NO_3 device, Abegg and Cumming (*Zeit. für Electrochemie*, **13**, 18, 1907) have determined the e.m.f. of the above cell for several concentrations of silver nitrate. Experiment shows that the electrode in c_2 is the positive pole of the cell when c_2 is greater than c_1. The nett e.m.f. E of the cell is the difference of the two single electrode e.m.f.'s e_3 and e_1.

Diagrammatically it may be represented as in Fig. 24. The system in equilibrium is now supposed to undergo a small virtual change, in which δF faradays of *positive* electricity are transported from left to right.

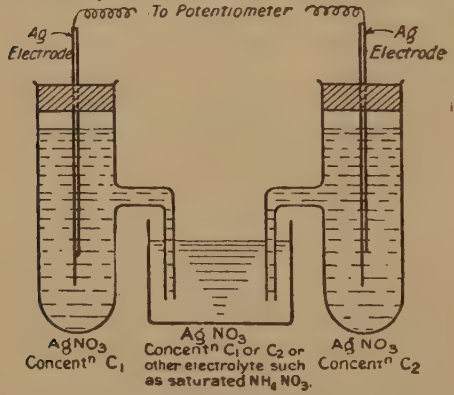

To Potentiometer
Ag Electrode
Ag Electrode
AgNO3 Concentn C1
AgNO3 Concentn C1 or C2 or other electrolyte such as saturated NH4NO3.
AgNO3 Concentn C2

FIG. 23.

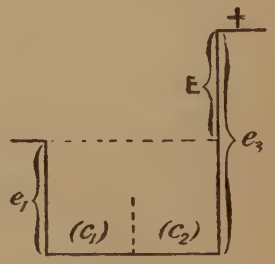


FIG. 24.

The electrical work is $E\delta F$, and since the electric force opposes the direction of motion (the electricity being of the positive kind), we must place a minus sign before the electrical work term in applying the principle of virtual work. Along with this electrical work some osmotic work is done. Since the solution pressure P of the *left*-hand electrode assists the motion of the positive electricity when being moved from left to right, and the osmotic pressure p_1 (corresponding to the concentration c_1 of Ag^+) opposes the motion, the osmotic work term will take the form $+ \delta x RT \log \frac{P}{p_1}$ or $\delta x RT \log \frac{C}{c_1}$, where δx stands as before for the number of gram ions of Ag^+ which carry the charge δF. Similarly, the work of transferring δx gram ions of Ag^+ *from* solution c_2 *to* the right-hand electrode will be $+ \delta x RT \log \frac{p_2}{P}$ or $+ \delta x RT \log \frac{c_2}{C}$, since in this case the osmotic pressure p_2 assists the motion of the δx gram ions from solution to electrode whilst the solution pressure P opposes. In such

logarithmic expressions the quantity in the denominator really has a minus sign before, since $\log \frac{x}{y}$ is identical with $\log x - \log y$, thereby indicating that in the virtual work process the term "x" assists the motion while "y" opposes it. Now applying the criterion of virtual work, *viz.* that the algebraic sum of all the work terms may be equated to zero, we obtain—

$$- E\delta F + \delta x RT \log \frac{C}{c_1} + \delta x RT \log \frac{c_2}{C} = 0$$

or since

$$\frac{\delta F}{\delta x} = nF$$

where n is the valency,

it follows that

$$E = \frac{RT}{nF} \log \frac{C}{c_1} + \frac{RT}{nF} \log \frac{c_2}{C}$$

or

$$E = \frac{RT}{nF} \log \frac{c_2}{c_1}.$$

A verification of this expression would involve a verification of the two single portions comprising it, *i.e.* a verification of the logarithmic relation—first deduced by Nernst—which exists between the concentration terms and the e.m.f.

Abegg and Cumming (*l.c.*) obtained the following results :—

Concentration of $AgNO_3$.	Ratio of the Ionic Concentration c_2/c_1.	$\frac{RT}{n} \log \frac{c_2}{c_1}$.	Observed Voltage.
$\frac{N}{10} : \frac{N}{100}$	9·0	0·0563 volts	0·0556
$\frac{N}{100} : \frac{N}{1000}$	9·6	0·0580 „	0·0579

It is usual to regard the faraday as itself the unit of electricity, and hence $f = 1$; so that we can write

$$E = \frac{RT}{n} \log \frac{c_2}{c_1}.$$

Calculation of the Liquid | Liquid Potential in Concentration Cells.

In the foregoing we have neglected the P.D. at the junction of the two liquids, *i.e.* where the two solutions meet, or we have employed a device which automatically reduces it to negligible dimensions. Where we do not employ the ammonium nitrate, or some such solution to annul the P.D., there are certain cases in which it is inaccurate to neglect it, *e.g.* in the case of normal alkali | normal acid. Before showing how such a P.D. may be calculated we shall take a simpler

case, namely, a cell made up of the same solute throughout ($AgNO_3$) but at different concentrations; just as in the case of the experiments of Abegg and Cumming already quoted, except that we shall make no attempt to annul the liquid potential difference, but indicate how it may be calculated when certain data have been given. If we have two silver nitrate solutions of different concentrations set up with silver electrodes, there are two ways in which the solutions will tend to equalise themselves. (1) The ions, + and −, tend in general to diffuse from the place of high concentration to that of low, this being a natural diffusion process across the boundary. If they travel at different speeds the excess of electricity, of the sign carried by the faster moving ion, is transferred across the boundary, so that the more dilute solution takes on the sign of the faster moving ion. An electric P.D. or "double layer" is formed, whose electric force finally checks further diffusion of the faster ion, and accelerates the motion of the slower ion going in the same direction, so that eventually both ions diffuse at the same speed, and so there is no further separation of electricity. Let this steady state be reached with P.D. $= e_2$ at the interface. (This state is reached practically instantaneously.) Now (2) in addition to this natural diffusion process, whereby the two solutions would be gradually brought to the same concentration, there is another method of attaining the same end, if the two solutions form part of a cell, as in Fig. 23, having two electrodes immersed in them, and the electrodes connected externally so as to allow current to pass. We can imagine such a current passing, with the result that silver dissolves off one electrode and is deposited on the other. Silver dissolves off the electrode immersed in the weaker solution, the silver of course dissolving in the ionic form, while at the same time an equivalent number of the silver ions in the stronger solution have deposited themselves on the electrode immersed in the stronger solution. The NO'_3 ions have of course travelled in the opposite direction to that of the current inside the cell (the direction of current being always taken as the direction in which the positive ions move). Thus the stronger solution has become somewhat weaker (due to the deposition of silver and the migration of NO_3 ions out of this compartment); the weaker solution has become more concentrated owing to the dissolving off of silver from the electrode into the solution, producing metallic ions, these ions meeting with their companion ions NO'_3 which have come from the other solution. In this way by allowing the cell to produce current, the two solutions tend to equalise their concentrations "by electrolysis," and when there is no longer a difference of concentration the e.m.f. of the cell falls to zero. In actual measurements of e.m.f., say by the potentiometer, practically no current is taken from the cell, so that there is no change in the actual initial concentrations. Under these conditions the e.m.f. measured should be steady and constant during the time taken for measurement. During this time of course the P.D. at the boundary of the two solutions is e_2. We will now proceed to calculate this quantity e_2 by imagining a virtual change in the system, namely, the passage of an infinitely small quantity

of current δF faradays through the cell from the ***weaker*** concentration to the *stronger*. This is carried across the boundary by silver ions going from the weak to the strong solution, and simultaneously by NO'_3 ions going from the strong solution to the weaker. This passage of electricity by means of electrolysis causes electric virtual work at the junction, namely, $e_2\delta F$ (volt faradays).

In the case of silver nitrate solutions experiment has shown that the mobility of the *anion*, which is directly proportional to its velocity v, is greater than the mobility of the cation, which is proportional to u. Hence since the *dilute* solution by the "natural" diffusion process across the liquid | liquid boundary takes on the electrical sign of the faster moving ion, it follows that the more dilute solution of $AgNO_3$ (c_1) is *negatively* charged compared to the more concentrated solution (c_2); that is, there is a rise of potential in passing from c_1 to c_2 which can be represented diagramatically thus—

$$\frac{}{c_1} \Big| \frac{c_2}{e_2}$$

In the case of two solutions of HCl, however, the rise of potential is in the opposite direction, since the cation ($H^{\cdot}$) travels much more quickly than the anion (Cl').

To return to the electrical work term $e_2\delta F$ (in the case of two silver nitrate solutions in contact). From the standpoint of virtual work this expression must be written with a minus sign, *viz.* $-e_2\delta F$, since the electric force *opposes* the direction of motion of *positive* electricity when the electricity is considered as passing from the weak to the strong solution. (Just the reverse statement is true in the case of two HCl solutions.) Now we have to consider the osmotic work terms simultaneously involved in the transfer of δF faradays of positive electricity. The fraction of the total charge δF carried by the positive ions is $\delta F\left(\frac{u}{u+v}\right)$ in one direction, namely, from weaker solution (c_1) to strong (c_2), where u is the velocity of the positive ions, and v the velocity of the negative ions in cms. per sec. under a given potential gradient ($\frac{u}{u+v}$ being numerically equal to the transport number $\frac{U}{U+V}$ of the cation). If the valency of the positive ion is n then 1 gram ion carries n faradays, but $\delta F\left(\frac{u}{u+v}\right)$ faradays have been transported by the positive ions, and hence this has involved the transfer of $\frac{1}{n}\left(\frac{u}{u+v}\right)\delta F$ positive gram ions (Ag^+). Similarly, if the anion has the same valeney n there must be $\frac{1}{n}\left(\frac{v}{u+v}\right)\delta F$ negative ions taking part in the process, the direction of motion of the negative ions being from the strong solution c_2 to the weaker c_1. If p_1 be the osmotic pressure of the solution c_1 (the weaker solution), and p_2 be the osmotic

pressure of c_2 (the more concentrated solution), then the osmotic work of transferring $\frac{\delta F}{n}\left(\frac{u}{u+v}\right)$ cations from p_1 to p_2 is—

$$\frac{\delta F}{n}\,\frac{v}{u+v}\,.\,RT\,.\,\log\frac{p_1}{p_2}.$$

Note that since p_1 assists and p_2 opposes the motion of the ions (from c_1 to c_2), the p_1 term appears as an essentially positive term, *i.e.* in the numerator, whilst p_2 appears with a negative sign, *i.e.* in the denominator of the logarithmic expression. Similarly, the osmotic work required to transfer $\frac{\delta F}{n}\left(\frac{u}{u+v}\right)$ anions from p_2 to p_1 (*i.e.* in the opposite direction) is—

$$\frac{\delta F}{n}\,.\,\frac{v}{u+v}\,.\,RT\,.\,\log\frac{p_2}{p_1}.$$

The total algebraic sum of all the work terms—since the process considered is virtual work—may be equated to zero. That is—

$$-e_2\delta F+\frac{\delta F}{n}\,\frac{u}{u+v}\,RT\log\frac{p_1}{p_2}+\frac{\delta F}{n}\,.\,\frac{v}{u+v}\,.\,RT\log\frac{p_2}{p_1}=0,$$

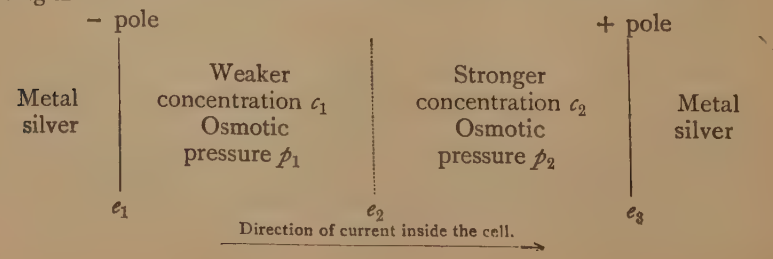
or
$$e_2=\frac{u-v}{u+v}\,\frac{RT}{n}\log\frac{p_1}{p_2}=\frac{v-u}{u+v}\,\frac{RT}{n}\log\frac{p_2}{p_1},$$

or
$$e_2=\frac{v-u}{u+v}\,\frac{RT}{n}\log\frac{c_2}{c_1}=\frac{V-U}{U+V}\,.\,\frac{RT}{n}\log\frac{c_2}{c_1}.$$

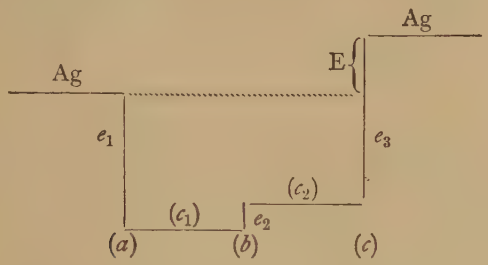
This expression gives the P.D. at the liquid | liquid interface in terms of the osmotic pressures or concentrations of the ions, and the absolute velocities or the mobilities of the ions (in the case of a binary electrolyte).

Expression for the Total E.M.F. of a Concentration Cell ("with Transport").

Again consider the silver nitrate concentration cell in which $c_2 > c_1$. The positive pole of the cell is the electrode in contact with the solution c_2. That is, current tends to flow inside the cell in the direction indicated, since the purpose of the flow of current is to equalise the concentrations c_1 and c_2, and this is evidently effected by silver dissolving off at the left-hand electrode and depositing on the right. Suppose the single P.D.'s as indicated are e_1, e_2, and e_3, the total e.m.f. being E—



Representing the single P.D.'s graphically, it will be seen that the following relation holds—



The net e.m.f. observed $E = e_3 + e_2 - e_1$.

Consider the following virtual change of the system. Let a current of δF faradays flow through the cell from left to right. The nett electrical work done is $- E\delta F$, the negative sign denoting that the direction of motion is *opposed* by the force. Adding this to the three separate osmotic work expressions corresponding to the three points (a), (b), and (c), and equating to zero, we obtain—

$$- E\delta F + \frac{\delta F}{n} . RT \log \frac{P}{p_1} + \frac{\delta F}{n} . \frac{u - v}{u + v} RT \log \frac{p_1}{p_2} + \frac{\delta F}{n} RT \log \frac{p_2}{P} = 0,$$

or
$$E = \frac{RT}{n} \log \frac{P}{p_1} + \frac{u - v}{u + v} . \frac{RT}{n} . \log \frac{p_1}{p_2} + \frac{RT}{n} \log \frac{p_2}{P}$$

$$= \frac{RT}{n} \log \frac{p_2}{p_1} + \frac{u - v}{u + v} \frac{RT}{n} \log \frac{p_1}{p_2}$$

$$= \frac{RT}{n} \log \frac{p_2}{p_1} \left(1 - \frac{u - v}{u + v}\right)$$

$$= \frac{2v}{u + v} . \frac{RT}{n} \log \frac{p_2}{p_1}$$

$$= \frac{2v}{u + v} \frac{RT}{n} \log \frac{c_2}{c_1}.$$

Note that if the P.D. e_2 had acted in the opposite sense, the final expression for E would have been—

$$\frac{2u}{u + v} \frac{RT}{n} \log \frac{c_2}{c_1}.$$

The expression $\frac{v}{u + v}$ is numerically identical with $\frac{V}{U + V}$ the transport number of the anion (NO_3). The following table gives the numerical values of the transport numbers of a few anions in the corresponding salts. Temperature 18° C.

Salt.	Concentration of Salt in Equivalents per Liter.					
	0·01.	0·02.	0·05.	0·1.	0·2.	0·5.
	Transport Number of the Anions.					
Potassium chloride ,, bromide ,, iodide Ammonium chloride	0·503	0·503	0·503	—	—	—
Sodium bromide ,, chloride	0·604	0·604	0·604	—	—	—
Lithium ,,	0·670	0·670	0·680	0·687	0·697	—
Potassium nitrate	—	—	—	0·497	0·496	0·492
Silver nitrate	0·528	0·528	0·528	0·528	0·527	0·519
Potassium hydroxide	—	—	—	0·735	0·736	0·738
Hydrochloric acid	0·174	0·174	0·174	—	—	—

It will be observed from the above table of values (experimentally determined by Hittorf's or other method) that in the case of a good many salts the transport number of the anion is in the region of 0·5. That is, the mobilities of these ions (namely, U and V) are nearly the same. This is the case, for example, with silver nitrate, in which $\frac{V}{U+V}$ is 0·528. Hence $\frac{2V}{U+V}$ is 1·056 or nearly unity. Hence, in the case of this salt, we might as a close approximation write the e.m.f. of the cell, namely E, as—

$$E = \frac{RT}{n} \log \frac{c_2}{c_1}.$$

This is the same thing as neglecting altogether the liquid | liquid P.D.; for the above expression is simply the e.m.f. of the two electrodes. In the case of alkalies and acids, however, the value of the transport number of the anion is far removed from 0·5 (thus in the case of potassium hydroxide the $\frac{V}{U+V}$ of the OH′ is 0·735, and in hydrochloric acid the value of $\frac{V}{U+V}$ for Cl′ is only 0·174), so that the factor $\frac{2V}{U+V}$ has a very great effect indeed upon the total e.m.f. of the cell in these cases. That is to say, when two solutions, say of hydrochloric acid, form part of a cell, the liquid | liquid P.D. cannot be neglected. To show the magnitude of such liquid | liquid potential differences, take the case of a cell consisting of—

Hg	0·01N. potassium chloride, saturated with Hg_2Cl_2	0·10N. potassium chloride, saturated with Hg_2Cl_2	Hg

The liquid P.D. in this case is due to 0·01 N.KCl meeting 0·10 N.KCl. The calculated P.D. is 0·0008 volts, *i.e.* exceedingly small. Now set up the same cell, but substitute hydrochloric acid for the potassium chloride in the two cases; the liquid | liquid P.D. now amounts to 0·0370 volt.

The formula which applies to the above cell is given on p. 158.

Note on the Means Employed to Eliminate Liquid | Liquid Potential Differences.

Mention has already been made of the insertion of a saturated solution of ammonium nitrate between the two solutions. This very probably eliminates the potential difference in the case of silver nitrate solutions, but it is by no means certain that it is of general application. The mechanism of the effect is quite obscure. Another method, due to Nernst, consists in having the same electrolyte (KNO_3 or KCl) present throughout the entire cell, the concentration of this added electrolyte being much greater than that of any other electrolyte present. In this way the current in the cell is carried mainly by the added electrolyte, and we are simply left with the electrode potentials. This is a more theoretically sound method, but it has the drawback of not being generally applicable (KCl could not be used, for example, with $AgNO_3$ owing to the formation of AgCl), and further if, say, potassium nitrate had been employed (say 1 normal) throughout the silver nitrate cell, we would be met with the difficulty that the extent of the dissociation of the silver nitrate would be altered owing to the presence of the NO'_3 ion from the potassium salt, and the extent of this dissociation alteration cannot be easily determined. We would not know therefore the numerical values to assign to c_1 and c_2 in the Nernst expression.[1] Mention should be made of a very ingenious method adopted by Cohen (*Zeit. für Electrochemie*, 1907) for obtaining by direct experiment the value of the liquid | liquid P.D. in the case of two solutions of zinc sulphate. The following cell was prepared:—

Zn	$ZnSO_4$ c_1	$ZnSO_4$ c_2	Zn
		π	

The total e.m.f. is E_1, where—

$$E_1 = \frac{RT}{2F} \log \frac{c_2}{c_1} + \pi$$

π being the liquid | liquid potential difference.

The e.m.f. of the following cell was then measured—

Hg	Hg_2SO_4 saturated in $ZnSO_4$ solution, concentration c_1	Hg_2SO_4 saturated in $ZnSO_4$ solution, concentration c_2	Hg
		π	

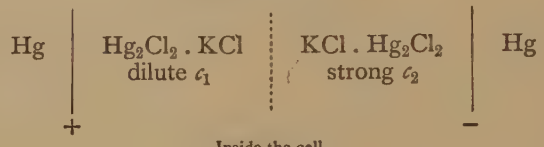
[1] *Cf.*, however, the conclusions arrived at by Brönsted (*Medd. K. Vetenskap. Nobelinst.*, 5, No. 25, 1-19 (1919) in connection with the applicability of the gas laws to mixtures of strong electrolytes when there is an ion in common.

The e.m.f. is E_2, where—

$$E_2 = -\frac{RT}{2F}\log\frac{c_2}{c_1} + \pi.$$

Adding E_1 and E_2 we get 2π, and hence π itself. [The negative sign in the second case comes in because in this case the electrode is reversible with respect to the anion SO''_4, and not with respect to the $Zn^{\cdot\cdot}$.]

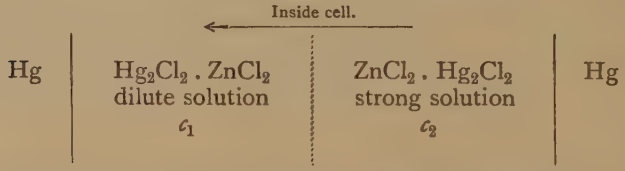
NOTE.—In the silver | silver nitrate concentration cell, the cell is reversible with respect to the cation $Ag^{\cdot}$. Cells can easily be set up reversible with respect to the anion. We have already considered one in dealing with Cohen's method of measuring the liquid | liquid P.D. A simple type of cell is represented by—



$$E = \frac{RT}{F}\cdot\frac{2U}{U+V}\log\frac{c_2}{c_1}$$

where c_1 and c_2 again refer to Cl' ions obtained from the KCl solutions.

Another such cell is represented by the combination—



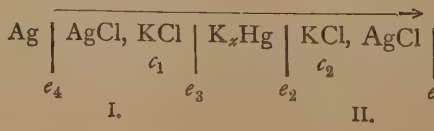
The total e.m.f. of this cell when the liquid | liquid P.D. is taken into account is

$$E = \frac{RT}{2F}\cdot\frac{3U}{U+V}\log\frac{c_2}{c_1}$$

where c_1 and c_2 refer to Cl' ions, *i.e.* the same expression as above except that the transport number of the cation is employed instead of the anion.

The E.M.F. of a Concentration Cell without Transport.

In this type of cell the two solutions do not come into contact with one another. Instead, the actual transport of material is effected by means of an intermediate metal which acts reversibly in the electrochemical sense with regard to both solutions. This type of cell is illustrated by the arrangement—



This particular cell would be called a potassium chloride concentration cell without transport. c_1 and c_2 denote the concentrations of the chlorine ions ($c_1 > c_2$). The intermediate electrode is in this case a potassium amalgam which may be employed, as was first shown by G. N. Lewis, as an electrode reversible with respect to potassium ions in aqueous solutions. The total e.m.f. E of the cell is made up of four single P.D.'s as indicated. We can write therefore—

$$E = e_1 - e_2 + e_3 - e_4.$$

Employing the solution pressure method adopted in the analogous case of a cell with transport we can evaluate E in the following manner.

Let [K] and [Ag] stand for the solution pressure of the amalgam and silver electrodes respectively. The osmotic pressure terms for the ions in the left-hand compartment of the cell will be denoted by the suffix I., those in the right-hand compartment by the suffix II. We can write therefore—

$$E = \frac{RT}{F}\left(\log_e \frac{Ag^+_{II}}{[Ag]} - \log_e \frac{K^+_{II}}{[K]} + \log_e \frac{K^+_I}{[K]} - \log_e \frac{Ag^+_I}{[Ag]}\right)$$

$$= \frac{RT}{F}\left(\log_e \frac{Ag^+_{II}}{Ag^+_I} + \log_e \frac{K^+_I}{K^+_{II}}\right).$$

In each compartment the solution is saturated with respect to silver chloride. Assuming the validity of the constancy of the ionic product we have—

$$Ag^+_I \times Cl^-_I = Ag^+_{II} \times Cl^-_{II}.$$

Hence

$$\frac{Ag^+_{II}}{Ag^+_I} = \frac{Cl^-_I}{Cl^-_{II}}$$

$$\therefore E = \frac{RT}{F} \log_e \frac{K^+_I \times Cl^-_I}{K^+_{II} \times Cl^-_{II}}.$$

But

$$K^+_I = Cl^-_I, \text{ and } K^+_{II} = Cl^-_{II}.$$

Hence

$$\frac{K^+_I}{K^+_{II}} = \frac{Cl^+_I}{Cl^+_{II}}.$$

Substituting this result in the above expression for the e.m.f. of the cell we have—

$$E = \frac{2RT}{F} \log_e \frac{Cl^-_I}{Cl^-_{II}}.$$

It will be observed that in this type of cell, one without transport, the transport number of the ion does not enter into the expression for the e.m.f. The e.m.f. is, however, just twice that which would be given by a potassium chloride concentration cell with transport in which the contact P.D. was neglected or annulled. This distinction must be emphasised. It will be observed further that the final expression for E does not involve the solution pressure of the silver or the amalgam

electrodes. The same value for the e.m.f. of the cell should be obtained, therefore, using amalgams of different composition. This conclusion is completely borne out by the results obtained by MacInnes and Parker (*Journ. Amer. Chem. Soc.*, **37**, 1445, 1915), who have measured the e.m.f. of the concentration cell discussed. Their results are given in the following table, the composition of the amalgam being expressed in potassium content.

E.M.F. of Potassium Chloride Concentration Cells without Transport at 25° C.

Ag | AgCl, solid KCl soln.	K_xHg Per cent.	KCl soln., AgCl solid | Ag	E.M.F. volts.
0·5 N	0·02	0·05 N	−0·10735
0·5 N	0·002	0·05 N	−0·10745
0·1 N	0·004	0·01 N	−0·10885
0·1 N	0·002	0·01 N	−0·10900
0·05 N	0·004	0·005 N	−0·11085
0·05 N	0·002	0·005 N	−0·11085

One of the most important distinctions between concentration cells, with and without transport, manifests itself when we consider the question of the amount of current (number of faradays) which must be allowed to pass through the cell in order to transfer one gram-equivalent of the electrolyte from one solution to the other.

In the case of cells with transport we have already seen that the actual amount of salt transferred when one faraday passes is less than one gram-equivalent. In the case of such a cell, having electrodes reversible with respect to the cation, the fraction of salt transferred is measured by the amount of *anion* which passes from the strong to the weak solution. The amount of salt transferred per faraday is, in fact, $v/(u + v)$ of one equivalent, where $v/(u + v)$ is the transport number of the anion. In the case of a similar cell with electrodes reversible with respect to the anion, the corresponding fraction is $u/(u + v)$. Hence to obtain the transfer of one gram-equivalent of salt it is necessary to allow $(u + v)/v$ faradays in the first case, or $(u + v)/u$ faradays in the second case to flow through the cell.

On the other hand, in the case of a cell without transport the passage of one faraday corresponds effectively to the transfer of one gram-equivalent of salt. Actually, there is no passage of salt ions from one compartment to the other. The effect is brought about by the electrodes and the intermediate metal. Thus, in the potassium chloride concentration cell, when the cell is giving one faraday of current, one gram-ion of silver dissolves off the electrode in compartment I., the equivalent of potassium being precipitated upon the amalgam. Since, however, the solution is already saturated with AgCl, the newly formed Ag^+ ion, and the corresponding number of Cl^- ions, "liberated" by the removal of the K^+, unite to form solid silver chloride. The compartment has therefore had its content diminished by one gram-

equivalent of KCl. In compartment II. the passage of the faraday causes one gram-equivalent of potassium in the ionic form to dissolve off the amalgam, and, at the same time, one gram-equivalent of silver (from the AgCl) is precipitated upon the right-hand silver electrode. Compartment II. experiences, therefore, an increase in KCl content of one gram-equivalent. The net effect is obviously the effective transfer of one gram-equivalent of KCl from one compartment to the other, per faraday.

A further conclusion may be drawn from these considerations. Let us think of the transfer of one gram-equivalent of salt from the strong to the weak solution, first in a cell with transport, and then in a cell without transport. Suppose that E_1 is the e.m.f. of the cell with transport, and E is the e.m.f. of the cell without transport. In the first cell, the amount of electrical energy corresponding to the transfer of one gram-equivalent of salt is $E_1 \times F \div$ (transport number of anion or cation). [If the cell is reversible with respect to the cation, the transport number of the anion must be employed, and *vice versa*.] In the second cell the amount of electrical energy is represented by $E \times F$. These two energy terms must be identical. Hence E_1/E = transport number of anion or of cation. This result, which is an important one, is arrived at in another way in the following section :—

Helmholtz's Method of Determining the Transport Number of an Ion from Electromotive Force Measurements.

This method, originally suggested by Helmholtz, was first applied in an exact manner by MacInnes and Parker, *loc. cit.*, during the course of an extended investigation of potassium chloride concentration cells. The principle of the method is as follows.

In the first place, let us imagine the following cell set up :—

$$\text{Ag} \;\Big|\; \underset{\text{I.}}{\text{AgCl, KCl}} \;\Big\|\; \underset{\text{II.}}{\text{KCl, AgCl}} \;\Big|\; \text{Ag}$$

This is a cell with transport, and has an e.m.f. of E_1 volts. This is given on the osmotic theory by the expression—

$$E_1 = \frac{2u}{u+v}\,\frac{RT}{n\mathfrak{F}}\log_e\frac{a_1c_1}{a_2c_2}$$

where $u/(u+v)$ is the transport number of the cation, K^+. It is necessary to employ this transport number and not that of the anion, because the cell as a whole is reversible with respect to the *anion*, Cl^-. c_1 and c_2 are the two concentrations of KCl, and, on the basis of the simple considerations which we have followed so far, a_1 and a_2 would represent the degrees of ionisation of the two KCl solutions, as determined by the conductivity method. We shall see later (Chap. VIII.) that a_1 and a_2 should be designated the "activity coefficients" of the ions, the quantities a_1c_1 and a_2c_2 representing the "activities" of the ions in the respective solutions. These activities are the quantities necessary to satisfy the e.m.f. equations; they are not identical with the concentrations of the ions as determined, say, by conductivity, except at

very great dilution. We shall not enter further into this matter at the present stage.

Now let us consider the following cell without transport :—

$$\mathrm{Ag} \left| \begin{matrix} \mathrm{AgCl,\ KCl} \\ \mathrm{I.} \end{matrix} \right| \mathrm{K}_x\mathrm{Hg} \left| \begin{matrix} \mathrm{KCl,\ AgCl} \\ \mathrm{II.} \end{matrix} \right| \mathrm{Ag}$$

This is a cell without transport, the e.m.f. of which is E. We have seen that this is given by the expression—

$$\mathrm{E} = \frac{2\mathrm{RT}}{n\mathrm{F}} \log_e \frac{a_1 c_1}{a_2 c_2}$$

where a and c have the same significance as before. On comparing the expressions for E_1 and E we see that—

$$\text{transport number of } \mathrm{K}^+ = \mathrm{E}_1/\mathrm{E} = \frac{\text{e.m.f. of cell with transport}}{\text{e.m.f. of cell without transport}}.$$

Had the above cells been reversible with respect to the cation, the ratio of the e.m.f. values would have given the transport number of the anion. The numerical values for the transport number of potassium ion as determined by MacInnes and Parker from the cells cited above are given in the following table :—

Comparison of the Transport Numbers of the Cation in KCl at 25° C., obtained by the E.M.F., Hittorf, and Moving Boundary Methods.

Concentrations of KCl.	E_1/E ratio.	Transport Number of K^+.		
		E.M.F.	Hittorf.	Moving Boundary.
0·5 : 0·05	53·57/107·4	0·498	0·496	—
0·1 : 0·01	54·00/108·9	0·496	0·496	0·493
0·05 : 0·005	54·70/110·85	0·494	0·496	0·493

It is evident that the electromotive force method gives values which are in good agreement with those obtained by other methods.

Helmholtz's Method of Calculating the E.M.F. of a Concentration Cell.

This method[1] in point of time is earlier than that of Nernst. Instead of following Helmholtz's original method of calculation, the simpler modification employed by Sackur in his book (*Thermochemistry and Thermodynamics*, English edit., p. 352) is here followed.

It will be observed that the process which actually takes place in a concentration cell, either with or without transport, and which gives rise to the e.m.f., is the tendency of the two solutions to become equal in concentration. If instead of transferring solute from one solution to the other we were to transfer solvent by isothermal distillation from weak to strong, the same equalisation of concentration could be obviously brought about. If we could evaluate the expression for this isothermal distillation work, we could equate it to the electrical work, for if we pass from one equilibrium stage to another by *any reversible*

[1] Helmholtz's paper referred to is translated into English in the *Phil. Mag.*, [5], 5, 348, 1878. (Other papers of Helmholtz are translated in the *Physical Society Memoirs.*)

path whatsoever, the work done is the same no matter what the particular path may have been.

The cell considered may be either with or without transport, the treatment being similar though not identical in the two cases. By way of illustration, we shall consider a cell with transport, such as the following:—

Ag	$AgNO_3$ c_1	$AgNO_3$ c_2	Ag

In the first place, let us imagine that the two solutions only differ in concentration by dc, the concentration of one solution of silver nitrate being c, the concentration of the other being $c + dc$. For the sake of convenience in discussion, we shall define the concentration of the solute as the ratio of the number of apparent moles of solute to total number of moles of solute and solvent; the solute is, of course, actually ionised to a large extent.

Suppose that one mole of silver nitrate is transferred electrically from the strong to the weak solution. Actually this is accomplished in the cell considered by metal dissolving off one electrode in the form of ions, a corresponding amount being deposited on the other electrode, whilst a certain amount of NO_3 ion crosses the boundary from the strong to the weak solution. In the cell considered the electrodes are reversible with respect to the cation, and consequently the passage of one faraday (F) involves the effective transfer of $v/(u + v)$ gram-ions of salt, this fraction being the transport number of the anion. Hence to cause the effective transfer of one mole of salt, it is necessary to allow $\frac{(u + v)}{v}$. F faradays to flow through the cell. The amount of electrical work involved in this is $\frac{(u + v)}{v}$F . dE volt faradays, dE being the e.m.f. of the cell in which the solutions only differ in concentration by dc. This transfer could just be balanced and annulled by the transfer in the same direction, *i.e.* from strong to weak, of n moles of water; where n is the number of moles of water present in either solution per mole of silver nitrate. Note that n may be taken as referring to either solution, since the solutions differ only by an infinitesimal amount. The vapour pressure of the solvent over the solution (whose solute concentration is c) is denoted by p, and the vapour pressure over the concentrated solution is denoted by $p - dp$. The work of isothermally distilling n moles of water between the two pressure limits is simply $-vdp$ or $-n\mathrm{RT}\frac{dp}{p}$, assuming that the vapour obeys the gas laws. Hence on equating the two work terms we obtain—

$$\mathrm{F} \cdot \frac{(u + v)}{v} dE = - n\mathrm{RT}\frac{dp}{p}.$$

Now n obviously depends on the concentration, for the concentration of solute in a solution is simply $\left(\frac{1}{n + 1}\right)$. Hence, if the two solutions

considered differ by finite amounts, the concentration of solute being c_1 and c_2, then $c_1 = \frac{1}{n_1 + 1}$ and $c_2 = \frac{1}{n_2 + 1}$; n_1 being the number of moles of water per mole of silver nitrate in the solution c_1, and n_2 the corresponding value of the water moles in c_2, we must integrate the above expression between the limits n_1 and n_2 in order to get the e.m.f. E. That is—

$$F\frac{(u + v)}{v} \int dE = EF\frac{(u + v)}{v} = - RT \int_{n_1}^{n_2} n\frac{dp}{p}.$$

To integrate this we must know of some relation between p and n. This is given by the approximate Raoult Law, namely, that—

$$\frac{p_0 - p}{p_0} = \frac{i}{n + 1}, \text{ or } p = p_0\frac{n + 1 - i}{n + 1}$$

where p_0 is the vapour pressure of water alone and i is the van 't Hoff factor. This has to be introduced into Raoult's expression to allow for the fact of ionisation. For dilute solutions of a binary electrolyte, such as $AgNO_3$, we may regard i as a constant, as a first approximation, having the value 2. It follows then that—

$$(n + 1 - i)dp/p = idn/(n + 1).$$

For dilute solutions n is large compared with either i or unity. Hence this expression becomes—

$$ndp/p = idn/(n + 1)$$

so that

$$E.F.\frac{(u + v)}{v} = - RT\int_{n_1}^{n_2} n\frac{dp}{p} = - RTi\int_{n_1}^{n_2} \frac{dn}{n + 1} = RTi \log_e \frac{n_1 + 1}{n_2 + 1}$$

$$= RTi \log_e \frac{c_2}{c_1}$$

since $c_1 = 1/(n_1 + 1)$ and $c_2 = 1/(n_2 + 1)$.

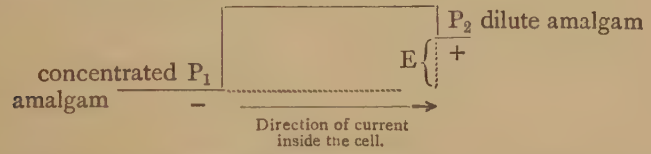
Hence $$E = i \cdot \frac{v}{u + v} \cdot \frac{RT}{F} \cdot \log_e \frac{c_2}{c_1} = \frac{2v}{u + v} \frac{RT}{F} \log_e \frac{c_2}{c_1}.$$

This is identical with the result obtained by the osmotic method for a concentration cell with transport, reversible with respect to the cation, the concentration of both solutions being such that practically complete dissociation may be assumed as a first approximation, and consequently the ratio of the salt concentrations is identical with the ratio of the concentration of the ions.

As regards the e.m.f. of concentration cells containing organic solvents relatively little is known owing to the difficulty of obtaining reliable values for the degree of ionisation. In acetone, silver nitrate seems to act in the way predicted by Nernst's formula (*cf.* Roshdestwensky and Lewis, *Trans. Chem. Soc.*, **99**, 2138 (1911); *ib.* **101**, 2094 (1912)). A short survey of the subject is given in an article by Carrara on the "Electrochemistry of Non-aqueous Solutions," *Ahrens Sammlung.*

Concentration Cells with Single Solutions.

A cell of this type has been realised and measured by G. Meyer (*Zeitsch. für physik. Chem.*, **7**, 447, 1891), in which the electrodes are amalgams of a given metal at two different concentrations. Thus, suppose some zinc is dissolved in mercury, the concentration of the zinc being c_1, and another amalgam is prepared in which the zinc is at concentration c_2, we can use these amalgams as two zinc electrodes (at different concentrations) dipping into a solution of zinc sulphate. Suppose that P_1 and P_2 are the respective solution pressures of the zinc in the two cases, P_1 being greater than P_2, and p_{Zn++} the osmotic pressure of the zinc ions in the solution, then we may represent the distribution of potential by the diagram—



Zinc has a very high solution pressure even in an amalgam and each electrode is negatively charged with respect to the solution. That is, the observed e.m.f. E is the difference of the two single P.D.'s. Carrying out a virtual work process involving the transfer of δF faradays of electricity through the cell from left to right, the total work terms are given by—

$$-E\delta F + \delta x RT \log \frac{P_1}{p_{Zn++}} + \delta x RT \log \frac{p_{Zn++}}{P_2} = 0$$

or since $\frac{\delta F}{\delta x}$ = the valency of the ion involved, in this case = 2 it follows that—

$$E = \frac{RT}{2F} \log \frac{P_1}{P_2}.$$

Assuming that the "solution pressure" of the zinc is proportional in each case to the concentration of the zinc in the amalgam, we can write—

$$E = \frac{RT}{nF} \log \frac{c_1}{c_2}.$$

This assumes that the metal is in the monatomic state.

The following results were obtained by Meyer in the case of zinc amalgams in contact with aqueous zinc sulphate :—

$t°$ C.	c_1.	c_2.	$E_{observed.}$	$E_{calculated.}$
11·6	0·003366	0·00011305	0·0419 volt	0·0416
18·0	0·003366	0·00011305	0·0433	0·0425
12·4	0·002280	0·0000608	0·0474	0·0445
60·0	0·002280	0·0000608	0·0520	0·0519

For a further account of similar cells and the questions which arise in connection with them, see Le Blanc, *Electrochemistry*, English edit., p. 185. It may be pointed out that arguing in an inverse way, one may employ the values of the e.m.f. obtained to determine the molecular (or atomic) state, *i.e.* the molecular weight, of the zinc in the amalgam.

Recently an investigation of thallium amalgam electrodes in a single thallium sulphate solution has been carried out by T. W. Richards and F. Daniels (*Journ. Amer. Chem. Soc.*, **41**, 1732 (1919)). In addition to e.m.f. measurements, carried out with the greatest accuracy over a wide range of amalgam concentrations at a series of different temperatures, measurements have also been made of the thermochemical behaviour of the amalgams, their densities and freezing points.

The following table gives some of the results obtained. The concentration of the thallium sulphate solution was approximately 2 per cent. The composition of the amalgams is also given in weight per cent., the e.m.f. values in millivolts at the temperatures 20°, 30°, and 40° C.

No. of Cell.	Amalgam Electrodes. Per Cent. Thallium.	E M.F. Millivolts.			dE/dT = Average Temp. Coefficient.
		20°	30°	40°	
I.	0·3315 : 1·704	45·550	46·937	48·326	0·0001388
II.	1·704 : 3·788	26·395	27·050	27·704	0·0000655
III.	3·788 : 4·935	9·763	9·968	10·168	0·0000203
IV.	4·935 : 10·019	29·480	29·971	30·467	0·0000493
V.	10·019 : 17·049	24·342	24·660	24·981	0·0000319
VI.	17·049 : 21·025	9·581	9·703	9·833	0·0000126
VII.	20·970 : 27·362	11·572	11·741	11·915	0·0000172
VIII.	27·362 : 34·029	8·681	8·844	9·001	0·0000160
IX.	34·029 : 42·858	8·174	8·360	8·547	0·0000187

For the first cell containing the most dilute amalgams the Nernst expression for the e.m.f., namely, $\frac{RT}{F} \log (c_1/c_2)$, is equal to 43 millivolts at 20° C., whilst the observed value is 45·5 millivolts. The agreement in this case is moderate. With the more concentrated amalgams the discrepancy between the calculated and observed values is considerable, the observed e.m.f. being in all cases much greater than that required by the concentration expression. Thus, in the case of the amalgams 10·019 per cent. : 17·049 per cent., the calculated e.m.f. at 30° C. is 13·88, whilst the observed is 24·66 millivolts.

Richards and Daniels have also shown the failure of the osmotic expression to apply quantitatively by considering the temperature coefficient of these cells. The reasoning is as follows:—

At any temperature T the e.m.f. should be given by—

$$E = \frac{RT}{F} \log (c_1/c_2).$$

Whence

$$dE/dT = \frac{R}{F} \log (c_1/c_2).$$

Again, at T = 273, we have $E_0 = \frac{R \times 273}{F} \log (c_1/c_2) = 273 \times dE/dT$.

Hence $\frac{1}{E_0}\frac{dE}{dT} = \frac{1}{273} = 0{\cdot}00366 = a$, the coefficient of expansion of a perfect gas. From the observed values of dE/dT and also of E_0 we can test whether this conclusion, derived from the osmotic expression, is correct. The results are given in the following table, in which the cell numbers are the same as those in the preceding table :—

Cell No.	$\frac{1}{E_0}\frac{dE}{dT}$	Cell No.	$\frac{1}{E_0}\frac{dE}{dT}$
I.	0·00325	VI.	0·00135
II.	0·00261	VII.	0·00149
III.	0·00215	VIII.	0·00191
IV.	0·00173	IX.	0·00238
V.	0·00135		

It is evident that the temperature coefficient of the cell is much less than that required by the simple osmotic theory. It is only in the case of the most dilute amalgams (cell I.) that $\frac{1}{E_0}\frac{dE}{dT}$ even approximates to the theoretical value, 0·00366. In the other cases the discrepancy is large. Richards and Daniels draw attention to the fact that the observed values in the preceding table pass through a minimum. The theoretical significance of these data is to be dealt with in a later publication.

As a result of freezing point measurements carried out with various amalgams, Richards and Daniels have shown that the compound Tl_2Hg_5 exists, its composition corresponding roughly to 29 per cent. of thallium. The compound melts at 14·9° C. Owing to dissociation one would scarcely expect the existence of this compound to affect seriously the e.m.f. values, especially in the more dilute region. The deviations from the osmotic expression can scarcely be attributed therefore to this compound.

Other Types of Concentration Cells.

Besides cells of the types already mentioned, cells can be constructed with electrodes giving anions directly (negatively charged ions). Thus the following cell, in which *Iodine* acts as the electrodes, has been realised.

Iodine electrode	I_2 in KI solution, giving KI_3 c_1	I_2 in KI solution, giving KI_3 c_2	Iodine electrode

In the actual setting up of this cell, it is sufficient to have a clean electrode of platinum inserted in each side, in contact with some solid iodine at the bottom of each vessel.

We may also have *gas cells*, *i.e.* cells in which a gas such as hydrogen or oxygen functions as the electrode. This is also realised by inserting a platinum electrode and allowing a stream of the gas to bubble through the solution in contact with the electrode, the bubbles also striking the piece of platinum. In such cases the platinum is chemically inert—it simply acts as a mechanical device to give rigidity to the gas electrode. Thus the following cell can yield a perfectly definite e.m.f., the e.m.f. depending on the logarithm of the ratio of the concentration of $H^{\cdot}$ ions as predicted by Nernst's Theory :—

Electrode H_2 (Platinum + Hydrogen gas)	Hydrochloric acid c_1	Hydrochloric acid c_2	H_2 electrode

As a practical point, it may be mentioned that the chief difficulty in setting up such gas cells is due to the fact that the platinum has already dissolved some oxygen from the atmosphere, and this in contact with OH' necessarily present in aqueous solutions, causes an oxygen concentration potential to be set up. It is necessary, therefore, to remove the oxygen as completely as possible. For details a textbook on Electrochemistry must be consulted. A very complete list of various sorts of cells, classified under seven heads, is given by W. D. Bancroft (*Journal Physical Chemistry*, **12**, 103, 1908).

The Calculation of Liquid | Liquid Potential Differences between Solutions containing non-identical Electrolytes.

The expression for the liquid | liquid P.D., namely—

$$e_2 = \frac{U - V}{U + V} \frac{RT}{nF} \log \frac{c_1}{c_2}$$

already deduced, is only applicable, of course, to the case in which we are dealing with one and the same binary salt ($AgNO_3$) at two different concentrations. We shall now take up the somewhat more complicated case of two binary electrolytes with different cations but the same anion. Thus, suppose that the following cell is set up—

Calomel electrode	HCl solution, Solution I.	KCl solution, Solution II.	Calomel electrode

We shall only consider the simplest possible case, namely, that the solutions of KCl and HCl are identical in concentration (c), and that the electrolytic dissociation of each salt is complete, and also that the valency of the ions is the same. This means that the chlorine ion has the same concentration, c gram ions per liter, throughout the cell. There is a liquid | liquid potential difference at the contact of solution I. and solution II., owing to the different mobilities of the $K^{\cdot}$ ions and

the $H^{\cdot}$ ions. We have to calculate what this will be. In the first place, however, it is necessary to see what assumptions are to be made regarding the *nature* of the transition layer between solution I. and solution II. There are two ways of looking at this. First we may consider with Planck [1] that the two solutions have been so brought together that the boundary is initially sharp. Natural diffusion will, however, commence and cause the sharpness to disappear. If mixture takes place by diffusion *alone*, the concentration in any layer is determined by two independent variables, the rates of diffusion of the salts. On the other hand, we can imagine, instead of a sharp boundary set up initially, that a connecting layer is formed by causing a part of the solutions to be mechanically mixed. This connecting layer is really a series of mixtures of the two solutions in all proportions, for in the body of solution I. the $K^{\cdot}$ ion concentration is zero, and in the body of solution II. the $H^{\cdot}$ ion concentration is likewise zero. This is the case considered by P. Henderson,[2] and as it seems to be more easily realised in practice than Planck's arrangement, and still more because it allows of a more simple mathematical treatment in calculating e_2, Henderson's method will be followed in the present case. Let us suppose that in the cell above described, where c represents the concentration of Cl' ions throughout, the mobility of the $H^{\cdot}$ ion is denoted by u_1, the mobility of the $K^{\cdot}$ ion by u_2, and the mobility of the Cl' ion by v. Suppose 1 faraday of electricity to pass through the cell. Consider a region in the connecting layer in which the solution consists of x parts of KCl and $(1 - x)$ parts of HCl, which is the same thing as saying that there are x gram ions of $K^{\cdot} + (1 - x)$ gram ions of $H^{\cdot}$ ions + 1 gram ion Cl', and suppose that 1 faraday of electricity is transferred from this region to another where x is now $x + dx$, and correspondingly $1 - x$ is now $(1 - (x + dx))$. This takes place by $H^{\cdot}$ ion and $K^{\cdot}$ ion travelling in the positive direction, Cl' in the negative. The fraction of 1 gram equivalent of each ion, which takes part in the transfer of the faraday is given by the expression—

$$\nu = \frac{\text{(concentration of the ion)} \times \text{(mobility of the ion)}}{\Sigma\,\text{(concentration)} \times \text{(mobility)}}$$

where the denominator denotes the sum of all terms involving the product of concentration into mobility of each ion present. In the particular case chosen—

$$\nu_{H^{\cdot}} = \frac{c(1 - x)u_1}{c(1 - x)u_1 + cxu_2 + cv} = \left\{\begin{array}{l}\text{fractional number of gram}\\ \text{equivalents of } H^{\cdot} \text{ ion.}\end{array}\right.$$

$$\nu_{K^{\cdot}} = \frac{cxu_2}{c(1 - x)u_1 + cxu_2 + cv} = \left\{\begin{array}{l}\text{fractional number of gram}\\ \text{equivalents of } K^{\cdot} \text{ ion.}\end{array}\right.$$

$$\nu_{Cl'} = \frac{cv}{c(1 - x)u_1 + cxu_2 + cv}.$$

[1] *Wied. Ann.*, **40**, 561, 1890.
[2] P. Henderson, *Zeitsch. physik. Chem.*, **59**, 118, 1907; *ibid.*, **63**, 325, 1908.

The osmotic work involved in this transfer is represented by dA where—

$$dA = \Sigma\nu \frac{-\,RT dp}{p}$$

where p is the osmotic pressure.

The total work A of the transfer of 1 faraday, when the whole layer is taken into account, is the integral of the above expression; the integration being carried out between the limits, when $x = 0$ to $x = 1$, for in the body of solution I. $x = 0$ and in the body of solution II. $x = 1$.

Now, since osmotic pressure is proportional to concentration in dilute solutions, we can write for the $H^{\cdot}$ ions:—

$$\frac{-\,dp}{p} = \frac{dx}{1 - x}$$

and for the $K^{\cdot}$ ions

$$\frac{-\,dp}{p} = \frac{-\,dx}{x}.$$

The difference in sign of dx in the two cases is due to the fact that in any two contiguous regions in the layer, if there is an increase in K, there is a corresponding decrease in $H^{\cdot}$, so that at any point the total concentration of cations is just equivalent to the anion Cl', which remains at constant concentration throughout. The work term in connection with the anion Cl' is obviously zero, since its concentration, and therefore its osmotic pressure, is constant. We thus obtain for the work term A the algebraic sum of the two work terms for $H^{\cdot}$ and $K^{\cdot}$ respectively, *viz.*—

$$\begin{aligned} A &= \int_0^1 \frac{(1 - x)u_1}{(1 - x)u_1 + xu_2 + v} \cdot \frac{RT}{1 - x} dx \\ &\quad - \int_0^1 \frac{xu_2}{(1 - x)u_1 + xu_2 + v} \cdot \frac{RT}{x} dx \\ &= RT(u_1 - u_2) \int_0^1 \frac{dx}{x(u_2 - u_1) + u_1 + v} \\ &= RT \log_e \frac{u_1 + v}{u_2 + v}. \end{aligned}$$

Putting $A = e_2 nF$

we get $$e_2 = \frac{RT}{nF} \log_e \frac{u_1 + v}{u_2 + v}.$$

[As a matter of fact, Planck's formula, to which reference will be made in a moment, reduces to this expression for the simple case chosen, *viz.* identity of one ion (Cl') in the two salts, and identity of concentration of the salts.]

The validity of the above formula has been examined recently by N. Bjerrum (*Zeit. für Electrochemie*, **17**, 391, 1911), in which the

experimental arrangement was such as to give a mechanically mixed boundary. Two calomel electrodes were employed in the cell, the solutions in contact being also chlorides at the same concentration on each side. The table below gives a few of Bjerrum's data.

The agreement between the last two columns is only moderate, and it is difficult to say how far this may be due to experimental error, for the total e.m.f.'s are very small. Planck (*l.c.*) has worked out the case in which the solutions in contact are different in concentration, and are likewise different in composition (*i.e.* no ions being necessarily in common), but the ions have all the same valency. The method of deduction will be found in the paper cited; it must suffice here simply to write down the formula obtained for the liquid | liquid potential difference.

Solution I.	Solution II.	Electrode P.D. Calculated by Nernst's Formula.	Liquid | Liquid P.D. Calculated by Henderson's Formula.	Sum of Calculated P.D.'s.	Total E.M.F. of Cell Observed.
0·1, N. HCl	0·1, N. KCl	− 0·0016	− 0·0276	− 0·0292	− 0·0278
0·1, N. NaCl	0·1, N. KCl	0·0005	0·0050	0·0055	0·0041
0·01, N. NaCl	0·01, N. KCl	0·0002	0·0048	0·0050	0·0039

Planck's formula—

$$e_2 = \Phi_1 - \Phi_2 = \frac{RT}{nF} \log_e \xi$$

where ξ is defined by the relation—

$$\frac{\xi u_1 c_1 - u_2 c_2}{v_1 c_1 - \xi v_2 c_2} = \frac{\log_e \frac{c_1}{c_2} - \log_e \xi}{\log_e \frac{c_1}{c_2} + \log_e \xi} \cdot \frac{\xi c_1 - c_2}{c_1 - \xi c_2}$$

where n, RT and F have the usual significance and u_1 and u_2 are the velocities of the cations, v_1 and v_2 the velocities of the anions, and c_1 and c_2 the corresponding ionic concentrations.

Planck's formula has been extended by K. R. Johnson (*Ann. der. Physik.*, **14**, 995, 1904) to the case in which the valency of the ions is *not* the same.

Henderson (*l.c.*) has likewise dealt with the general case, in which the two solutions differ in concentration, and have not necessarily any ion in common, and the ions not being necessarily of the same valency. This method is more readily followed than that of Planck, but there is not space to give it here. The final expression reached is—

$$e_2 = \frac{RT}{F} \cdot \frac{(U_1 - V_1) - (U_2 - V_2)}{(U'_1 + V'_1) - (U'_2 + V'_2)} \log_e \cdot \frac{U'_1 + V'_1}{U'_2 + V'_2}.$$

Where in the one solution—

$$U_1 = u_1c_1 + u_2c_2 + \text{etc.}$$
$$V_1 = v_1c_1 + v_2c_2 + \text{etc.}$$
$$U'_1 = u_1n_1c_1 + u_2n_2c_2 + \text{etc.}$$
$$V'_1 = v_1n_1c_1 + v_2n_2c_2 + \text{etc.}$$

the corresponding quantities for the second solution are denoted by U_2, V_2, U'_2, V'_2.

This formula may be illustrated by some of Bjerrum's data (*loc. cit.*)—

Solution I. Normality.	Solution II. Normality.	Electrode P.D. Calculated by Nernst's Formula.	Liquid | Liquid P.D. Calculated by Henderson's Formula.	Sum of Calculated P.D.'s.	Observed E.M.F. of Cell.
0·01 HCl	0·10 KCl	0·0562	− 0·0101	0·0461	0·0458
0·01 NaCl	0·10 KCl	0·0570	− 0·0028	0·0542	0·0553
0·09 KCl, 0·01 HCl	0·10 KCl	− 0·0002	− 0·0050	− 0·0052	− 0·0041
0·1 NaCl	0·09 KCl, 0·01 HCl	0·0007	0·0097	0·0104	0·0083

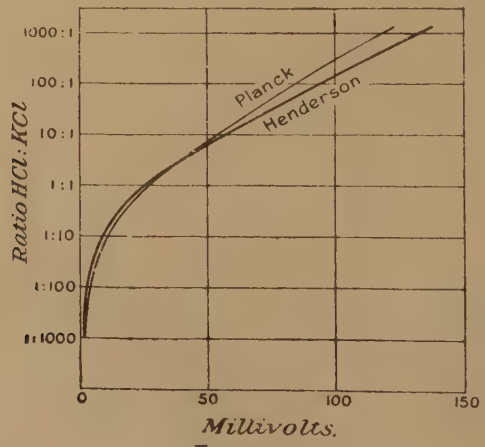


FIG. 25.

A critical study of the relative applicability of Planck's and Henderson's formulæ has been undertaken by A. C. Cumming (*Trans. Faraday Soc.*, **8**, 86, 1912; *ibid.*, **9**, 174, 1913). A final conclusion has not yet been reached, though the evidence seems to point to the greater applicability of Henderson's formula. As a matter of fact, although the views taken regarding the nature of the separating boundary differ widely in

the two methods of treatment, the numerical values of the liquid | liquid P.D. are not correspondingly very widely different. The graph on previous page (Fig. 25) taken from Cumming's paper (1913) shows the liquid | liquid P.D. in the case of HCl and KCl solutions of different concentrations calculated by Planck's and Henderson's formulæ respectively. It will be seen that the differences become appreciable only when the ratio of HCl to KCl becomes very large.

The applicability of Planck's formula has been investigated by Fales and Vosburgh (*Journ. Amer. Chem. Soc.*, **40**, 1291 (1918)) using cells of the type—

Hg	Hg_2Cl_2, KCl	KCl	HCl	H_2

The contact P.D. between the two KCl solutions may be easily calculated by Nernst's formula, the single P.D.'s. of the electrodes being also known, whence an approximate determination of the contact P.D. between KCl and HCl may be made. A few of the results may be quoted.

Using decinormal HCl, at 25° C., in contact with x normal KCl (where x can be varied), the following contact P.D. values in volts are obtained—

x =	0·1	1·0	1·75	2·5	3·5	4·1	
P.D. obsd. =	0·0270	0·0076	0·0047	0·0022	0·0006	zero	volts
P.D. calcd. =	0·0282	0·0112	0·008*	0·007*	0·006*	0·0055*	volts

by Planck's formula.

(Values marked * are taken from the curve given in the paper cited.)

It will be observed that the discrepancy between the calculated and observed values increases as the concentration of the KCl increases. Perhaps the most important practical result arrived at is that there is no measurable contact P.D. between a saturated solution of KCl (4·1N) and HCl solutions ranging in concentration from 0·1N to 1·0N.

Standard Electrodes or Standard Half Elements.

Since the e.m.f. of any cell is necessarily made up of at least two parts corresponding to the electrodes, it is necessary, for the purposes of comparison in many cases, to make one of the electrodes and the liquid in which it is immersed (such being called the half-element) possess a constant value. This electrode must be easily and conveniently set up. It must give, under the same conditions of concentration and temperature, the same potential differences, *i.e.* it must yield reproducible values in the hands of different operators. It must likewise have as small a temperature coefficient as possible. One half element used frequently for this purpose is the calomel standard electrode. It consists essentially of some very pure mercury acting as the electrode, external connection being made by means of a platinum wire immersed in the mercury. The liquid in contact consists of a solution of KCl saturated with calomel Hg_2Cl_2; saturation being guaranteed by having a layer of calomel (mixed with mercury to ensure the absence of mercuric chloride $HgCl_2$) placed over the mercury. The half

element is usually made in the shape illustrated (Fig. 26). When 1 normal potassium chloride is employed the electrode is called the "normal calomel electrode". When $\frac{N}{10}$ KCl is used it is called the "decinormal calomel electrode". The absolute values of these two electrodes are known approximately, that of the "normal calomel" being 0·56 volt, the "decinormal calomel" being 0·61 volt.[1] The mercury in each case is positively charged with respect to the solution of mercury ions produced from the calomel. When used as a reference standard, the P.D. of the "normal calomel" is set arbitrarily at zero and other half elements referred to it. Another standard electrode consists of a hydrogen electrode (the gas being at atmospheric pressure) immersed in a normal solution of $H^{\cdot}$ ions (a little over normal HCl solution). Taking this as zero P.D., the actual P.D. of the calomel is + 0·283 volts. That is, if we connect up a normal hydrogen electrode with a normal calomel, the cell will give a current, the current passing inside the cell *from* the hydrogen electrode to the mercury. The mercury is therefore the positive pole of the cell, the e.m.f. of which is 0·283 volt. Taking the hydrogen as zero, it is obvious that on the same scale the calomel is + 0·283 volt. A list of such standards is given by F. Auerbach (*Zeit. für Elektrochemie*, **18**, 13, 1912).

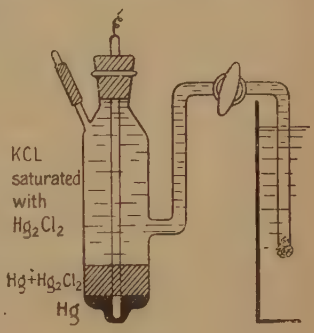


FIG. 26.

The Electrolytic Potential ("*E.P.*").

This is the P.D. at a reversible electrode (say silver in contact with $AgNO_3$ solution), when the concentration of the ions is normal. The expression for a single potential of this kind is, as we have already seen, given by—

$$\pi = \frac{-RT}{nF} \log_e \frac{P}{p} = \frac{-RT}{nF} \log_e \frac{C}{c},$$

if c = concentration of the ions is unity (in 1 normal ionic solution), $\log c = 0$, and hence the electrolytic potential "E.P." is given by—

$$\text{"E.P."} = \frac{-RT}{nF} \log_e C = \frac{-RT}{nF} \log_e \frac{P}{RT}.$$

This is the nearest approach we can make to a physical interpretation of P, *i.e.* P is a quantity whose logarithm is proportional to the electrolytic potential of the electrode in question. The following table gives the electrolytic potentials of a few electrodes, the values in the first column being referred to the "normal calomel" electrode as a zero electrode, the values of the second column referring to the "normal hydrogen" as a zero electrode.

[1] For a discussion of the methods of determining these absolute values and the sources of error inherent in the determination, see Lehfeldt, *Electrochemistry*, in this series of Textbooks.

ELECTROLYTIC POTENTIALS.

Electrode.	E.P. "Normal Calomel" Electrode = 0.	E.P. "Normal Hydrogen" Electrode = 0.
Platinum	ca + 0·580	ca + 0·863
Silver	+ 0·515	+ 0·798
Mercury	+ 0·467	+ 0·750
Copper	+ 0·046	+ 0·329
Hydrogen	− 0·283	∓ 0·000
Tin	ca − 0·475	ca − 0·192
Zinc	− 1·053	− 0·770
Potassium[1]	− 3·48	− 3·20
Oxygen	+ 0·110	+ 0·393
Iodine	+ 0·315	+ 0·628

The positive sign means that on joining up the cell, one-half being the standard, the other half the metal under investigation in a normal solution of its ions, the current flows *inside* the cell, from the standard electrode to the metal electrode, *i.e.* the metal electrode is the positive pole of the cell. The negative sign of course indicates that the electrode examined is the negative pole of the cell.

Mechanism of Electrolytic Conduction and Discharge of Ions on Electrodes.

It might appear at first sight that this would be of a simple character, but as a matter of experience, the question is by no means easy to deal with experimentally. When we consider the simplest case in which a metal electrode, like silver, is in contact with a solution containing a considerable quantity of its ions, say silver ions, the process of the discharge of an ion is represented by the passage of an electron from the electrode on to the ion, which thereby loses its electric charge and is precipitated upon the metal. Thus—

$$Ag^+ + \ominus \rightarrow Ag \text{ metal}$$

the electron being denoted by the symbol $\ominus$. If the reaction is one of ion formation, we have to assume that the reaction is—

$$Ag_{metal} \rightarrow Ag^+ + \ominus.$$

The presence of the electron symbol appearing on one side of the reaction equation denotes a transfer of electricity, and the reaction can only take place when current is allowed to flow. The direction of current is taken as the *reverse* of the direction of transfer of electrons, so that in the first case the current flowed from solution to electrode, and in the reverse sense in the second case.

[1] Metals like potassium, which react with water, have to be determined indirectly. *Cf.* G. N. Lewis and Kraus, *J. Amer. Chem. Soc.*, 32, 1463 (1910), for measurements in the case of sodium.

Electrolysis of a Complex Salt.

Potassium silver cyanide solution is a very convenient solution to use for the deposition of silver at the cathode. There are, however, very few actual $Ag^{\cdot}$ ions which could react with the electron passing out from the cathode, when the ion is in close proximity according to the equation—

$$Ag^{+} + \ominus \rightarrow Ag.$$

According to Wilsmore, what happens is that the complex silver containing anion—the salt being $2K^{+}$ and $Ag(CN)_4^{--}$ although it is naturally streaming away from the cathode, reacts with the electron at the cathode thus—

$$Ag(CN)_4^{--} + 2\ominus \rightarrow Ag + 4C\bar{N}.$$

Remember that this is the *cathode* process, two electrons passing *from* the electrode to the solution. Naturally the $C\bar{N}$ formed starts to go towards the anode. When electrolysis is prolonged there may be no longer sufficient $Ag(CN)_4^{--}$ ions to so react (partly because they have been used up as above, and partly because they have migrated too far from the electrode (cathode)), and the $K^{\cdot}$ begins to discharge, making the cathode liquid alkaline. At the *anode*, if it is of silver, the above reaction is just reversed, *viz.* :—

$$Ag + 4C\bar{N} \rightarrow Ag(CN)_4^{--} + 2\ominus$$

the two electrons being given up to the electrode. Probably also the complex $Ag(CN)_4^{--}$ can further react.

Anions may thus react at both cathode and anode. In these cases considered, where a silver electrode either produced $Ag^{\cdot}$ ions, or had Ag deposited upon it from a solution containing $Ag^{\cdot}$ ions, the electrode is called a *non-polarisable* one. That is to say, if we set up a silver | silver nitrate cell consisting of two silver electrodes in one and the same solution of silver nitrate, and cause electrolysis by impressing an external e.m.f. upon the cell from a battery or machine, we would find on suddenly causing the electrolysis to cease, and then connecting the two silver electrodes through a voltmeter that there was no back e.m.f. produced. The cell would be simply in the electrically neutral state in which it was at the beginning. It is most important to remember that the osmotic theory of e.m.f. refers to cells, each electrode of which is non-polarisable or perfectly reversible. If, on the other hand, we electrolysed a dilute sulphuric acid solution (by means of an externally applied e.m.f.), using platinum electrodes, and then cut off the external current and joined up the electrodes as before we would find quite a considerable e.m.f. The cell is then said to be polarised. What has happened is that the hydrogen and oxygen gases which have been produced by the electrolysis have formed a hydrogen and oxygen electrode respectively. The existence and magnitude of this back e.m.f. may be at once observed, if the externally applied e.m.f. be too small, for if it be less than the polarisation e.m.f. the process of electrolysis would automatically stop. A platinum electrode dipping into sulphuric acid

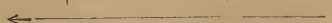
is an example of a non-reversible or polarisable electrode. Of course once the platinum has become charged up with either hydrogen or oxygen it will again function as a reversible hydrogen or oxygen electrode, the platinum, however, not entering into the phenomenon as such. In the above case, however, there is polarisation of the cell as a whole, for one electrode is an oxygen electrode, the other a hydrogen electrode.

A polarisable electrode can in many cases be converted into a non-polarisable electrode by means of the addition of a *depolariser*. Thus mercury in contact with potassium chloride solution is a polarisable electrode. If, however, we saturate the solution with mercurous chloride (allowing as a guarantee of saturation, a layer of calomel to be on the surface of the mercury), the electrode mercury | mercurous chloride + potassium chloride is now non-polarisable. This particular electrode, as already described, is known as the calomel electrode. Suppose that positive current is passing from the solution into the mercury. This means that electrons are passing from the mercury into the solution. An electron leaves the mercury and attacks a mercury ion (present from the calomel), thereby discharging it so that it is deposited as metallic mercury. This means that at the same moment a chlorine ion discharges itself at the second electrode, or causes some secondary reaction to take place at this second electrode, which causes the discharge of an electron on to the latter electrode. In this way current passes through the cell, but there are never at any moment any unbalanced ions present in the solution or solutions composing the cell. As regards the mechanism of electrolysis, attention should be drawn to some rather unexpected results obtained by F. Haber and J. Zawadzki (*Zeit. für physik. Chem.*, **78**, 228, 1911) in the case of solid compressed salts as "electrolytes".

Electrometric Method of Measuring the Solubility of Sparingly Soluble Salts.

In Vol. I. the electrical method of determining the solubility of a salt such as silver chromate by measurement of the conductivity has already been described. In the case of a salt like silver chloride the solubility is so very small that the conductivity method would be a somewhat inaccurate one. By means of electromotive force measurements, however, the solubility of this salt can be determined with a high degree of accuracy. Thus if the following concentration cell be set up—

Ag electrode	$AgNO_3$ $\frac{N}{100}$	Saturated NH_4NO_3	$\frac{N}{10}$ KCl saturated with silver chloride	Ag



the current is found to flow from right to left inside. The silver chloride, which we can regard as completely dissociated, gives rise to

$Ag^{\cdot}$ and Cl' ions. If L is the solubility product $[Ag^{\cdot}][Cl']$, then the solubility S is $\sqrt{L}$. Now in the presence of $\frac{N}{10}$ KCl (which is added in order to make the solution conduct), the concentration of the Cl' ions is approximately 0·1 N (correctly speaking we should allow for the fact that the degree of dissociation is not complete), and practically all the Cl' present comes from the KCl, for the actual quantity of Cl' produced by the AgCl is quite negligible in comparison. Hence the solubility S is equal to $\sqrt{[Ag^{\cdot}] \times 0{\cdot}1}$. If we could determine the $[Ag^{\cdot}]$ the value of S could be at once calculated. If the above cell gives an e.m.f. of E, it is clear that—

$$E = \frac{RT}{nF} \log_e \frac{0{\cdot}01}{x}$$

where x is the number of gram-equivalents per liter of $Ag^{\cdot}$ ions in the KCl + AgCl solution. The factor $\frac{RT}{nF}$ multiplied by the factor converting natural logarithms into logarithms to the base 10, has the value 0·058, at ordinary temperatures, if the e.m.f. is to be given in volts. That is—

$$E_{volts} = 0{\cdot}058 \log_{10} \frac{0{\cdot}01}{x}$$

from which x is easily calculated, and hence the solubility product L, and from that the solubility S. In this way it was found that the solubility of AgCl in water at 25° C. amounts to $1{\cdot}2 \times 10^{-5}$ gram-equivalents per liter. (See Goodwin, *Zeitsch. physik. Chem.*, **13**, 641, 1894.) The solubility of AgCl might also be determined by measuring the e.m.f. of the cell—

Ag	$\frac{N}{10}$ KCl saturated with AgCl	Cl

The chlorine electrode consists of platinum foil saturated with chlorine gas. If both electrodes produced cations, the nett e.m.f. would be the difference of the two single potential differences. Since, however, the chlorine electrode produces anions, the two electrodes assist one another, and the nett e.m.f. of the cell is the sum of the two single potentials. That is—

$$E = 0{\cdot}058 \log \frac{c_{Ag^{\cdot}}}{C_{Ag}} + 0{\cdot}058 \log \frac{c_{Cl'}}{C_{Cl}}$$

and since $- 0{\cdot}058 \log C_{Ag}$ and $- 0{\cdot}058 \log C_{Cl}$ represent the electrolytic potentials of these two electrodes, which we can denote by π_{Ag} and π_{Cl} respectively, we can write—

$$E = \pi_{Ag} + \pi_{Cl} + 0{\cdot}050 \log c_{Ag^{\cdot}} \cdot c_{Cl'}$$

Knowing E, π_{Ag}, π_{Cl} and $c_{Cl'}$ (which is $\frac{N}{10}$), we obtain $c_{Ag'}$, and as before the solubility product of dissociated silver chloride. If the above cell is allowed to give current, the reaction inside the cell is the formation of silver chloride, first in the form of ions, which, of course, unite to give solid silver chloride, since the solution is already saturated with respect to this salt. The salt is formed at the expense of the silver and chlorine electrodes respectively.

The process considered is simply the formation of solid silver chloride from its constituents, of which the electrodes are formed. Since the cell is a reversible one in the electrochemical sense, and since we can imagine the process carried out infinitely slowly and therefore reversibly in the thermodynamic sense, it follows that the work done is maximum work and is therefore independent of the path followed. Hence if we substitute alcohol, say, in place of the water, we would expect the same e.m.f. E as before, for E is a measure of the maximum work done. The value of E is therefore independent of the nature of the solvent. Hence the expression—

$0{\cdot}058 \log \frac{c_{Ag'} \times c_{Cl'}}{C_{Ag} \times C_{Cl}}$ is independent of the solvent, or writing $c_{Ag'} \times c_{Cl'} = L_{AgCl}$, the solubility product of silver chloride, $\frac{L_{AgCl}}{C_{Ag} \times C_{Cl}}$, is also independent of the nature of the solvent. But L_{AgCl} certainly varies with the nature of the solvent, for the solubility itself varies. Hence $C_{Ag} \times C_{Cl}$ varies with the solvent. That is, in general, the solution pressure of an electrode varies with the nature of the solvent. This conclusion makes it even more difficult to visualise what we mean by solution pressure, for it is evidently not characteristic of the electrode alone, as it depends also upon the solvent.

Electrometric Determination of the Valency of Ions.

The classic illustration of how the valency of an ion can be determined from e.m.f. measurements is that of the mercurous ions [Hg_2^{++}] investigated by Ogg (*Zeitsch. physik. Chem.*, **27**, 285, 1898).

The mercurous ion may be represented by either Hg^+ or [Hg_2^{++}]. The method of investigating whether the mercurous ion was a single atom carrying one charge or two atoms together carrying two charges, is determined by calculating n in the e.m.f. expression—

$$\frac{RT}{nF} \log \frac{c_2}{c_1}.$$

Suppose the following cell is set up—

Hg	$\frac{N}{2}$ Mercurous nitrate dissolved in $\frac{N}{10}$ nitric acid	$\frac{N}{20}$ Mercurous nitrate dissolved in $\frac{N}{10}$ nitric acid	Hg

+ pole ← Inside. — pole

The nitric acid is present to prevent hydrolysis of the mercury salt. Suppose the concentration of mercury ions in $\frac{N}{20}$ mercurous nitrate is represented by c_1 and that in the $\frac{N}{2}$ by c_2. Neglecting the liquid | liquid P.D., we can write the e.m.f. E of the cell in the form—

$$E = \frac{RT}{nF} \log \frac{c_2}{c_1} = \frac{0{\cdot}058}{n} \log_{10} \frac{c_2}{c_1}.$$

For the actual case mentioned E was observed to be 0·029 volt. Taking as a first approximation that $\frac{c_2}{c_1} = \frac{20}{2} = 10$, then $\log_{10} \frac{c_2}{c_1}$ = unity, and—

$$0{\cdot}029 = \frac{0{\cdot}058}{n}, \text{ or } n = 2.$$

That is the valency of the *mercurous* ions is two. That is the mercurous ion carries two charges, and we must therefore represent it by Hg_2^{++} since we know that one equivalent of mercury is united to one equivalent of NO_3 in mercurous nitrate. The proper formula for a molecule of mercurous nitrate is therefore $Hg_2(NO_3)_2$. We infer, therefore, that Hg_2Cl_2 is the correct formula for calomel.

Electrometric Determination of the Hydrolysis of Salts.[1]

In dealing with various methods of measurement of the hydrolysis of salts by water in Vol. I., reference was made to a method depending upon e.m.f. determinations. This method will now be described. It consists essentially in using a hydrogen electrode in the solution of the salt, which is partly hydrolysed, the other half of the cell being a calomel element, the two halves of the cell being connected by means of a saturated solution of ammonium nitrate which was taken as annulling the liquid | liquid potential difference. From the e.m.f. value obtained, the concentration of $H^{\cdot}$ ions present in the salt solution is calculated, and hence the degree of hydrolysis. This method is particularly suitable when the concentration of $H^{\cdot}$ ions is very small, in fact in cases in which other methods would be inapplicable. Its applicability is, however, limited by the fact that it cannot be employed to determine the hydrolysis of salts, the metal of which is more noble than the hydrogen itself, *i.e.* it cannot be used in the case of those metals like copper, silver, mercury, gold, which would be precipitated upon the platinum electrode, an equivalent quantity of hydrogen passing into the ionic state, but it can be used for salts of metals such as aluminium, nickel, cobalt, zinc, cadmium magnesium, barium; also one cannot employ the hydrogen electrode in the case of cations such as ferric^{+++} ions, which are partly reduced by the hydrogen, or in the case of reducible anions such as NO'_3, ClO'_3. It has been used with success by Denham

[1] *Cf.* H. G. Denham, *Journ. Chem. Soc.*, 93, 41, 1908. Also Loomis and Acree, *Journ. Amer. Chem. Soc.*, 46, 621, 1911.

(*loc. cit.*) in determining the hydrolysis of such salts as aluminium chloride, aluminium sulphate, nickel chloride, nickel sulphate, cobalt sulphate, and aniline hydrochloride amongst others. These salts in which the base is weaker than the acid, are hydrolysed by water, giving rise to some of the free base undissociated and some free acid, which is largely dissociated so that the solutions react acid. Such salts of polyvalent metals can exhibit the phenomenon of progressive hydrolysis into several stages, as already pointed out in Vol. I., Chap. V. Each one of these stages has its own characteristic hydrolysis constant. For a discussion of the relation of these to one another Denham's paper must be consulted. As an illustration of the method of applying the hydrogen electrode to the measurement of hydrolysis, we shall take the case of aniline hydrochloride, which is hydrolysed according to the equation—

$$C_6H_5NH_2HCl + H_2O = \underset{\substack{\text{Anilinium hydroxide}\\ \text{mainly } \textit{un}\text{dissociated}}}{C_6H_5NH_3OH} + \underset{\substack{\text{completely}\\ \text{dissociated in}\\ \text{dilute solution.}}}{HCl}$$

If 1 gram-mole of aniline hydrochloride is dissolved in v litres of water and a fraction x is hydrolysed, then $\frac{x}{v}$ represents the concentration of anilinium hydroxide and likewise of the acid produced, which is identical with the concentration of $H^{\cdot}$ and Cl' since the acid is practically completely dissociated. Regarding the water concentration as constant and therefore really taken account of in the hydrolysis constant K, we have for the above reaction when equilibrium is reached—

$$K = \frac{x^2}{(1 - x)v}$$

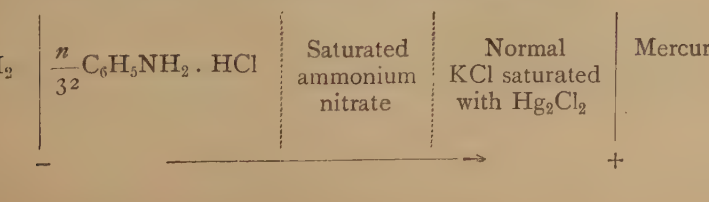
as already explained in Vol. I., Chap. V. Knowing v we have only to obtain $\frac{x}{v}$, which is numerically identical with the concentration of $H^{\cdot}$ ions, to be able to calculate K. The single potential π at the hydrogen electrode can be written in the form—

$$\pi = \frac{RT}{nF} \log \frac{c_{H^{\cdot}}}{C},$$

or, since $-$ RT log C is simply the electrolytic potential (E.P.) which we can denote by π_0, and is also known from other measurements, we can write—

$$\pi = \pi_0 + \frac{RT}{nF} \log c_{H^{\cdot}} = \pi_0 + \frac{RT}{nF} \log \frac{x}{v}.$$

In a particular case when the aniline hydrochloride was made up to $v = 32$ liters (at 25° C.) the observed e.m.f of the cell—



was 0·4655 volt; the current *inside* the cell passing from left to right, so that the normal calomel was the positive pole of the cell. Now it is known that the "normal calomel" possesses a potential difference between the mercury and calomel-potassium chloride solution of + 0·56 volt[1] approximately, the mercury being positively charged with respect to the solution; hence it follows that the P.D. of the hydrogen electrode must be 0·56 − 0·4655 = + 0·095 volt, the hydrogen electrode likewise being positive with respect to the solution in contact with it. Hence—

$$0{\cdot}095 = \pi_0 + \frac{RT}{nF} \log \frac{x}{v}.$$

The "absolute" value of the electrolytic potential of hydrogen, *viz.* π_0 as measured against the "normal" calomel electrode (when this electrode is taken not as zero but as + 0·56) is + 0·277 volt, that is, if we join a hydrogen electrode in contact with a solution of normal concentration of hydrogen ions, with a normal calomel electrode (ammonium nitrate saturated solution being interposed) the calomel is the positive pole of the cell, the current flowing inside from hydrogen to calomel, and the total e.m.f. of the cell is + 0·283 volt. [Note, if we take the calomel as zero, it is obviously 0·283 volts higher than the normal hydrogen, and therefore the normal hydrogen on this scale would be represented by − 0·283 volt, as has been done in the table of Electrolytic Potentials (E.P.) values already given.] It follows therefore, since $n = 1$ for hydrogen ions, and $\frac{RT}{F}$ for 25° C. is 0·059 [the unit of energy being the volt-faraday, and the natural logarithm being transformed to logarithm to the base 10], that—

$$0{\cdot}059 \log_{10} \frac{x}{v} = 0{\cdot}0945 - 0{\cdot}277 = - 0{\cdot}1825.$$

Hence $\frac{x}{v}$ = concentration of $H^{\cdot}$ ions = 0·000807 $\left\{\begin{matrix}\text{gram ions of } H^{\cdot} \text{ per} \\ \text{liter.}\end{matrix}\right.$

Since complete hydrolysis of the aniline hydrochloride would produce a value for $\frac{x}{v}$ of $\frac{1}{32}$ (assuming complete dissociation of the hydrochloric acid), the percentage hydrolysis of the aniline hydrochloride at dilution $v = 32$ is—

$$\frac{0{\cdot}000807}{\frac{1}{32}} \times 100 = 2{\cdot}58.$$

Further the hydrolytic constant K is given by—

$$K = \frac{(0{\cdot}000807)^2 \times 32}{1 - (0{\cdot}000807 \times 32)} = 0{\cdot}000021.$$

In the following table Denham's figures are given for the percentage hydrolysis of aniline hydrochloride, and the hydrolytic constant for a series of dilutions—

[1] On the so-called absolute scale, *cf.* p. 174.

Dilution of Salt. v.	Observed E.M.F. of Cell.	π Single P.D. of Hydrogen Electrode.	% Hydrolysis.	Hydrolytic Constant $K \times 10^6$.
16	0·4567	+ 0·1033	1·82	2·1
24	0·4609	0·0991	2·32	2·3
32	0·4655	0·0945	2·58	2·1
			Mean = 2·16	

The value of the percentage hydrolysis for $v = 32$ is 2·58, which agrees well with that found by Bredig by the electrical conductivity method, namely, 2·61.

Gravity Cells and Centrifugal Cells
(*cf.* R. C. Tolman, *Proc. Amer. Acad.*, 1910).

In general one may define a cell as representing a set of conditions in which available or free energy of some kind may be converted into electrical energy. That the force of gravity (and therefore centrifugal force) could conceivably give rise to an electromotive force follows from the fact that the passage of current in a cell involves the actual transfer of matter through the solution. Thus, suppose that we had a vertical tube filled with $AgNO_3$ solution with silver electrodes at the top and bottom and that a current is passed from the lower to the upper electrode. This necessitates the relatively heavy silver ions being raised against gravity, whilst the lighter nitrate ions are lowered. The net effect produced by the current consists in the lifting of a certain mass of material, whereby work is done against gravity. This work must correspond to a certain e.m.f. which will oppose the passage of the current in the direction considered.

This effect, which is a very small one, has actually been observed by several investigators, notably by Des Coudres, who, in order to magnify the effect, substituted centrifugal action in place of gravity, the tube containing the solution being rotated and the e.m.f. measured. In Des Coudres' arrangement the e.m.f. observed was of the order 100 to 200 microvolts (1 microvolt = 10^{-6} volts). He abandoned the centrifugal method, however, owing to the erratic results obtained, in favour of measurements with specially constructed gravity cells, in which the two electrodes were placed at a vertical distance apart of 377 cms. The following table contains some of Des Coudres' results obtained with such gravity cells. The e.m.f. is expressed in microvolts per cm. difference in height, the error estimated by Des Coudres not exceeding $\pm$ 0·009 microvolt. From the expression for the e.m.f. produced by gravity (or by centrifugal action) the transport number of one of the ions—in Des Coudres' experiments the anion—can be calculated. This expression will be given later. It is important to note that the transport number thus obtained is the Hittorf number, not the true transport

number obtained, say, by the use of a reference substance, as in Washburn's method. The column headed T_a gives the values of the transport number of the chlorine ion as obtained by Des Coudres, the final column containing Hittorf's values. (The negative sign before certain of the e.m.f. values denotes that the cation is less massive than the ion, and consequently the direction of the e.m.f. is the reverse of that in the other cases.)

Salt.	Per cent. Concentration.	E.M.F.	T_a	T_a Hittorf.
KCl	16·8	+ 0·0510	0·50	0·52
NaCl	19·9	− 0·0315	0·66	0·65
LiCl	17·3	− 0·109	0·77	0·75
HCl	3·56	− 0·0218	0·150	0·175
$BaCl_2$	17·0	+ 0·170	0·64	0·65

The agreement between the values in the last two columns is satisfactory.

The problem of measuring the e.m.f. produced by centrifugal action was first successfully solved by Tolman (*loc. cit.*). The success depended essentially upon the mechanical arrangements whereby very high rotation frequency could be realised without undue introduction of extraneous effects which would influence the observations. For the details of the experimental arrangement the original paper must be consulted. It is proposed only to summarise here the results.

In the first place it is necessary to deduce the expression for the e.m.f. The following treatment is due to Tolman:—

Consider a vertical tube of height h filled with the solution and provided with electrodes at the top and bottom. If E is the P.D. in volts between the upper and lower electrodes produced by the action of gravity, then by allowing one faraday of electricity to flow we would obtain the external work EF (volt-faradays), or joules, equivalent to $10^7 \times$ EF ergs. The passage of this electricity through the solution is accompanied however by the transfer of a certain nett weight of material from the upper electrode to the lower. It is evident that the external work (10^7 EF ergs) will just be sufficient to restore the solution to its original condition, that is, will do the work of raising the transferred material back from the lower electrode to the upper. For the sake of definition let us suppose that the electrolyte is a solution of an iodide, and that we are using iodine electrodes, consisting in practice of platinum electrodes with a small quantity of iodine dissolved in the solution. If now we let one faraday flow through the solution we know that one atomic weight of iodine, or M_i grams will be liberated at the anode or upper electrode and will disappear from the lower electrode, and at the same time there will be a change in the ratio of salt to water at the two electrodes, such that $T_c M_s$ grams of salt will have apparently been transferred from the anode to the cathode, where T_c is the Hittorf transport number of the cation and M_s is the molecular weight of the

salt. In order, therefore, to restore the solution to its original state of uniform concentration, it is necessary to raise $T_c M_s$ grams of salt from the lower electrode to the upper one, at the same time lowering one atomic weight of iodine. If we raise or lower these substances *through* the solution, it is evident that they will be buoyed up by a force equal to the weight of the volume of solution which they displace. Hence, if g is the acceleration of gravity, and d the density of the solution, the downward force acting respectively on the salt and the iodine will be—

$$gT_cM_s(1 - v_sd), \text{ and } gM_I(1 - v_{I_2}d),$$

where v_s and v_{I_2} are the "partial" specific volumes of the substances. (The "partial" specific volume of a solute is defined as the increase in volume of the solution when one gram of the solute is added to a quantity of the solution so large that the addition causes no appreciable change in concentration. The calculation of this quantity from the density of the solution is considered in detail by Tolman, *loc. cit.*) Equating the external electrical work to the work done against these forces in transferring the substances from one electrode to the other we have the desired relation—

$$10^7EF = hg[T_cM_s(1 - v_sd) - M_I(1 - v_{I_2}d)] \quad . \quad (1)$$

If, instead of using a gravity cell, we rotate the solution n times per second with electrodes at r_1 and r_2, since the centrifugal force acting on one gram at any radius r is $4\pi^2n^2r$, the work done in carrying one gram from r_1 to r_2 is—

$$\int_{r_1}^{r_2} 4\pi^2n^2rdr = 2\pi^2n^2\ (r_2^2 - r_1^2),$$

and the equation for the e.m.f. becomes—

$$10^7EF = 2\pi^2n^2(r_2^2 - r_1^2)[T_cM_s(1 - v_sd) - M_I(1 - v_{I_2}d)] \quad . \quad (2)$$

It is evident that the e.m f. which is to be measured is proportional to the factor hg or $2\ \pi^2n^2\ (r_2^2 - r_1^2)$. In the experiments of Des Coudres with gravitation cells, the factor, hg, was 360,000, whilst with his rotation experiments the corresponding factor was 583,000. In Tolman's centrifuge experiments the value of the factor was as high as 114,000,000.

It may be pointed out that, looking at the phenomenon from the molecular standpoint, the fact that an electromotive force is *spontaneously* produced by centrifugal force is striking evidence for the existence of free ions in an electrolyte, or at least of a certain degree of electrical polarisation in the molecules.

The general experimental arrangement used by Tolman consists of a steam turbine with vertical shaft driving the rotator which contains the tubes of solution. Electrical connection with the electrodes in the solution is made through mercury contacts.

The solutions examined were KI, NaI, LiI, and HI, with iodine electrodes. In general, the order of magnitude of the e m.f. obtained was 2 to 6 millivolts. Tolman showed experimentally that the e.m.f. is proportional to the square of the number of revolutions per sec. as equation (2) requires.

Tolman goes on to consider transport numbers in the light of the e.m.f. values obtained. As already explained in Vol. I. Washburn has determined the true transport number of an ion, and has shown that it differs from the ordinary or Hittorf number. The Hittorf transport number gives, however, the number of equivalents of salt which apparently disappear in the neighbourhood of one electrode, and appear at the other when one faraday is sent through the solution, and hence the Hittorf number gives the amount of salt which must be moved in order to restore the solution to its original condition of uniform concentration. From a consideration of the deduction of equation (2) it is evident that the Hittorf number is the one measured by the centrifugal method. Rewriting equation (2) we obtain for the transport number of the cation (in Tolman's cells)—

$$T_c = \left[\frac{4{\cdot}895 \times 10^{10}E}{(r_2^2 - r_1^2)n^2} + M_I(1 - v_{I_2}d)\right] \div M_s(1 - v_sd).$$

Using the average value for E/n^2 for each salt, the following values of T_c have been obtained ($M_I = 126{\cdot}9$, and $v_{I_2} = 0{\cdot}2376$) :—

Solution.	$\frac{E}{n^2} \times 10^6$.	$r_2^2 - r_1^2$.	M_s	v_s.	d_s.	T_c.
$\frac{M}{1}$, KI + $\frac{M}{100}$, I_2	657·1	846	166	0·284	1·115	0·486
$\frac{M}{1}$, NaI + $\frac{M}{100}$, I_2	889·0	849·3	149·9	0·244	1·110	0·385
$\frac{M}{1}$, LiI + $\frac{M}{100}$, I_2	1183	849·3	133·9	0·2605	1·096	0·268
$\frac{M}{1}$, HI + $\frac{M}{50}$, I_2	375·9	846·2	127·9	0·282	1·090	0·816

The probable error in T_c is estimated by Tolman to be ± 0·010. It is of interest to compare these values with the transport number obtained by other methods. Very few data are available in the case of iodides with the exception of the measurements of Dennison (*Trans. Faraday Soc.*, **5**, 165 (1909)). The Hittorf number may also be calculated from conductivity results at infinite dilution. The following table contains these comparative results :—

Hittorf Transport Number of the Anion.

Salt.	Centrifugal Method.	From Conductivity at Infinite Dilution.	Dennison.
KI	0·514	0·507	0·514
NaI	0·615	0·604	0·624
LiI	0·732	0·665	—
HI	0·184	0·174	—

CHAPTER VIII.

Chemical Equilibrium in homogeneous systems (Dilute solutions continued)—Mechanism of osmotic pressure—Semipermeability of membranes—Modern theory of dilute solutions of electrolytes—Abnormal behaviour of ions and undissociated molecules—Activities of ions—Activity coefficient and degree of ionisation—Activity of molecules.

Mechanism of Osmotic Pressure.

In dealing with osmotic pressure and the various relations which depend upon it, we have not examined hitherto with care what the possible molecular mechanism of the pressure may be. We have spoken of a dissolved substance as functioning as a gas, and the simple concept that a dissolved substance in dilute solution not only acts like a gas in respect of its osmotic pressure but is in effect identical with a gas, has been accepted by many investigators as correct. Others take the view, however, that in spite of the applicability of the gas laws to very dilute solutions of a non-electrolyte, the resemblance between a solute and a gas is only an apparent one. In short, the osmotic pressure is not regarded as due to a bombardment of the membrane by the molecules of the solute; it is doubtful whether any very large number of the solute molecules ever reach the semipermeable membrane at all. The important conclusion to which the balance of evidence seems to point is that the osmotic pressure is primarily connected with the solvent, and only secondarily with the solute.[1] It is important to see how this view of the mechanism of the phenomenon may be reconciled with the well-established fact that the solute (a non-electrolyte) in dilute solution appears to function as a gas with a high degree of accuracy. It may be well to point out that the molecular bombardment view of osmotic pressure, though usually ascribed to van 't Hoff, cannot in justice be so ascribed, for van 't Hoff was careful, in his original paper, to suggest two possible modes of operation without deciding between them (*cf.* Vol. I., Chap. IV.). It is also necessary to point out that the various osmotic relationships already deduced do not help us to decide what the actual mechanism of the osmotic effect may be. These relations will not be affected by discarding the molecular bombardment concept and substituting for it the alternative view which is about to be discussed. This is true even of the simple deduction given in Chap IV., Vol. I., of the connection between osmotic pressure and the lowering of vapour pressure, for the osmotic

[1] This is emphasised, for example, in Washburn's *Principles of Physical Chemistry*.

pressure was simply treated as equivalent to a hydrostatic pressure hpg. The same is true, for example, of the more exact logarithmic relation deduced in Chap VI., Vol. II.

Before passing on to consider the newer concept of the problem, we may refer to the osmotic pressure of colloidal solutions and emulsions in view of Einstein's use of the term, osmotic pressure, in deducing the expression which was experimentally verified by Perrin (*cf.* Chap. I, Vol. I.).

The only kind of pressure which we can ascribe to emulsion and colloid particles is a true bombardment pressure as a result of the kinetic energy possessed by the particles, this energy being energy of thermal agitation. Owing to the relatively small number of these particles present in unit volume this pressure is exceedingly small. Its origin, on the new view of osmotic pressure proper, is different from that exhibited by solutions of crystalloids. In fact a colloidal solution resembles a gas much more closely than does a solution of a crystalloid. A gas consists of particles, molecules, sparsely distributed throughout a given space, that is in presence of a medium of an exceedingly fine grained structure (the ether). Similarly a colloidal solution or an emulsion consists of particles sparsely distributed in presence of a fine grained structure, consisting of molecules of the liquid medium which are much smaller in size than the colloid or emulsion particles themselves. The true resemblance between colloidal solutions and gases forms the basis of Svedberg's considerations already referred to in Chap. I, Vol. I. Instead of using the term osmotic pressure for this kinetic bombardment pressure exhibited by colloid solutions it would be preferable to employ the term kinetic or thermal pressure. The existence of thermal pressure is due to the equipartition of kinetic energy between the molecules of the medium and the colloid particles at a given temperature. Naturally the same equipartition occurs between the molecules of the solvent and the molecules of the solute in the case of a true solution. Owing to equipartition the mean kinetic energy is $3/2$ RT per mole; this, however, does not necessarily prove that osmotic pressure in *true* solutions is due to the thermal agitation of the solute molecules. In the account given of Perrin's work (Chap. I., Vol. I.) we should therefore substitute the term thermal pressure or kinetic pressure in place of the term osmotic pressure, for as will be shown below, the new view of osmotic pressure attributes the effect in the case of a true solution to quite other causes.

The principal argument against the gaseous bombardment view of osmotic pressure is the fact that a solution is a true liquid in the full sense of the term. That is, between the molecules forces of cohesion exist which are of very large magnitude, owing to the close packing of the molecules and the very limited unoccupied or free space. These large forces are exerted upon solvent and solute molecules alike. (The solute molecules are also hydrated probably, but this does not enter into the question at present.) Of course, in the interior of a liquid the forces of cohesion cancel out, and the molecules are quite free to move

within their limited space. At the surface, however, there is a resultant inward pull exerted upon every molecule which tends to prevent their escape. For this reason the vapour pressure of the solvent never rises to excessive values, and in many cases the vapour pressure of the solute is too small to be measured. That is, the bombardment pressure, whether of the solvent molecules or of solute molecules actually exerted upon the surface of the containing vessel is a relatively small quantity. We may regard the question, as has recently been done by Tinker (*Phil. Mag.*, **32**, 295, 1916; *ibid.*, **33**, 428, 1917) from the standpoint of Dieterici's equation (*cf.* Chap. II., Vol. I.).

First of all let us consider the pure solvent alone. According to Dieterici, a pure liquid possesses what may be called a liquid pressure, which is identical with the thermal pressure already referred to—in the case of a liquid which can function as a solvent, we shall use the term *solvent pressure* instead of liquid pressure. This solvent pressure is denoted by the symbol π. π is connected with the *free* space in the liquid and with the temperature by the ordinary gas law. The solvent pressure is the pressure exerted on unit area *in the interior* of the liquid. It is a quantity which cannot be measured directly, for any direct measurement involves a surface of discontinuity at which the observed bombardment pressure is very much less than π. If the volume of the liquid is V and the actual volume occupied by the molecules is b, the free space in the pure solvent is $(V - b)$ and the following relation holds—

$$\pi(V - b) = RT.$$

π is a kinetic or bombardment pressure identical in origin with the pressure actually asserted by a *gas*. Although π is a real quantity, it cannot be measured directly for the reasons given above. In liquids, b is nearly identical with V itself. It follows, therefore, that π is a very large quantity. The term R refers to the number of gram-molecules of liquid present in the observed volume, V. According to Dieterici, the *observed* boundary pressure p of the liquid is connected with π by the relation—

$$p = \pi e^{-A/RT}$$

where A is the work done by the molecule in reaching the surface. Since A is large in general, the exponential term is small, that is, p is small compared with π.

Now let us consider a dilute solution of a non-volatile solute. In the interior of the solution the *solute* exerts a bombardment pressure π_s given by the relation—

$$\pi_s(V - b') = R_sT$$

where b' is the volume actually occupied by the molecules of the solvent and solute, the term $(V - b')$ denoting the free space in the solution, and R_s refers to the number of gram-molecules of *solute* present in volume V. In general R_s is much smaller than R previously referred to for the pure solvent alone, because in a given volume of solution there are many more molecules of solvent than there are molecules of

solute. Further, if the solute is practically non-volatile, this involatility indicates that the backward pull at the surface exerted upon the molecules of the solute is so great that the solute can exert practically no bombardment pressure on the surface. It is reasonable to believe that this is true also at the membrane.

If this be the case, the osmotic pressure observed is not accounted for by bombardment of the membrane by the molecules of the solute We must seek therefore some other physical basis for the phenomenon of osmotic pressure. We shall first of all consider the simplest case, that of an ideal solution. An ideal solution according to Tinker (*l.c.*) is one in which the molecular volume and properties of the *solvent* remain unchanged on addition of the solute. The fundamental idea of Tinker's theory is, that *the solvent pressure in a solution is less than that in the pure solvent itself.*

To make this clear, let us think of equal volumes of two gases A and B. If the gases are mixed and if the resulting volume is just twice the original volume of either, it follows that the partial pressure of either constituent (say A) in the resulting mixture, is just one-half of its value in the original state. It is to be observed that this diminution in the pressure exerted by A is brought about, although the effective space occupied by any single molecule is just the same before and after mixing, *i.e.* the space per molecule = total number of molecules / total volume occupied; and in the case considered we have doubled the number of molecules and doubled the volume at the same time.

To return to the case of the mixture of two liquids or of a solution formed from a solid and a liquid, in the ideal case considered the partial liquid pressure of the solvent is diminished for exactly the same reason that the partial pressure of the gas A was diminished. If therefore the solvent and solution are separated by a membrane permeable to solvent, impermeable to solute, the solvent pressure on the pure solvent side is greater than the solvent pressure on the solution side, and consequently some solvent passes into the solution, *i.e.* osmosis occurs.

Further, we can apply an additional external pressure to the solution and so prevent osmosis taking place. This applied pressure is numerically the osmotic pressure of the solution, and in fact the method is employed to determine osmotic pressure experimentally. By compressing the solution we obviously diminish the free space in the solution and therefore cause the solvent pressure in the solution to rise until it is equal to the solvent pressure in the pure solvent and no further osmosis takes place, *i.e.* the solvent is now passing in and out of the membrane at the same rate. This is the position of equilibrium.

It is well known that liquids are compressible only to a slight extent. It follows that in liquids there must be very little free space, *i.e.* the b term is very nearly the same as the V term itself. If this were not so, it would be inconceivable that the application of a pressure of a few atmospheres by means of a piston or an inert gas could sensibly affect the free space and therefore the value of the liquid pressure. To indicate the relative order of magnitude of V and b for liquids the

following approximate values are quoted from a table given by Traube (cf. Lewis, *Trans. Faraday Soc.*, **7**, 1911). V stands for gram-molecular volume in c.cs.

Substance.	V.	*b*.	V − *b*.
Water	18	17·4	0·6
Methyl alcohol	39·5	33	6·5
Carbon disulphide	58·8	47·5	11·3
Acetone	72·4	56·3	16·1
Methyl acetate	77·4	61·3	16·1
Benzene	86·5	70·3	16·2

On the above theory the osmotic pressure of an ideal solution depends upon the fact that there is a difference between the values of the solvent pressure in the pure solvent and in the solution respectively. Let us denote the solvent pressure in the pure solvent by π and its value in the solution by π'. We have been considering an ideal solution as defined by Tinker. (It will be shown later that in non-ideal solutions, *i.e.* those in which the molecular volume of the solvent is altered as a result of addition of solute, the resulting osmotic pressure is a more complex phenomenon, involving the intrinsic or cohesion tension of the solvent as well as its liquid thermal pressure. For the present we are dealing with the ideal case, however.)

The above statement that the osmotic pressure of an ideal solution involves the difference of π and π' does not mean that the osmotic pressure P is simply $\pi - \pi'$. This is not the case. To find the connection between P and π let us carry out the following simple thermodynamical cycle at constant temperature.

Consider a solvent and a solution each of practically infinite size. Suppose one mole of solvent is transferred from the pure solvent to the solution. Work is done in the transfer which can be reckoned in terms of the solvent pressure. The maximum work is $RT \log \pi / \pi'$, provided the general relation, $\pi (V - b) = RT$, holds good, as is assumed in Tinker's treatment of the problem. The gram-molecule of solvent is now removed from the solution reversibly by means of a semipermeable membrane, osmotic work being done *upon* the system. The volume of one gram-molecule of the solvent is supposed to be the same, *viz.* V_1, in the solution as it is in the solvent, since the solution is an ideal one. The maximum osmotic work done upon the system is therefore PV_1. The gram-molecule may now be added without further work to the original solvent and the cycle is complete. Since it is isothermal the total work is zero, or—

$$RT \log \pi / \pi' - PV_1 = 0,$$

or

$$P = \frac{RT}{V_1} \log \pi/\pi' \quad . \quad . \quad . \quad . \quad (1)$$

Since the solution is dilute π does not differ greatly from π' and we can write: $\log \pi/\pi' = (\pi - \pi')/\pi'$.

Hence $$P = \frac{RT}{V_1} \cdot \frac{\pi - \pi'}{\pi'} \quad . \quad . \quad . \quad . \quad (1a)$$

For a given solvent at a given temperature $R'T/V_1$ is a constant, and therefore $P \propto (\pi - \pi')/\pi'$. This is the relation between the osmotic pressure P and the solvent pressure π in the case of an ideal solution. This view attributes the phenomenon of osmotic pressure to the solvent primarily.

It has already been stated that at osmotic equilibrium, *i.e.* when the solution is under an applied external pressure identical in magnitude with the so-called osmotic pressure of the solution, the solvent pressure is the same in the pure solvent and in the solution, provided the solution is an ideal one. This may be demonstrated as follows. Suppose one mole of solvent is transferred isothermally and reversibly from the pure solvent to the solution. The maximum work is RT log π/π'. When equilibrium exists this work term must be zero, that is, when $\pi = \pi'$, *i.e.* when the solvent pressure is the same on both sides of the membrane.

In the foregoing, we have been considering ideal solutions, *i.e. those in which there is no contraction or expansion of the solvent on mixing*—although as will be shown later this does not *necessarily* mean that the final volume is exactly the sum of the two separate volumes of the constituents prior to mixing—*and further no heat effects accompany the act of mixing*. In the ideal case, which is very nearly realised by dilute solutions of sucrose in water, it is an experimental fact that the gas law is obeyed with a high degree of accuracy. The demonstration that the applicability of the gas law is to be anticipated (in the limiting case) on the basis of Tinker's theory, *viz.* that osmotic pressure is essentially due to a modification in the solvent pressure, will be given later.

In the case of non-ideal solutions, it has been shown by Bancroft (*Journ. Physical Chem.*, **10**, 322, 1906) that even when the solutions are dilute, the gas law is not nearly obeyed, if marked heat effects accompany the admixture. If heat is evolved on mixing, the osmotic pressure is considerably greater than that calculated on the basis of the gas law; if heat is absorbed, the observed osmotic pressure is considerably less than that calculated.

It is almost impossible to see how such statements can be explained on the basis of the bombardment view of osmotic pressure, the bombardment being due to molecules of the solute. On the other hand, considerable modification in the value of P is to be anticipated on the basis of the solvent pressure theory of osmotic pressure, when marked volume changes accompany admixture; and marked volume changes are accompanied by marked heat effects. This point will now be considered.

Equation (1) may be taken as characteristic of an ideal solution. It gives the relation between P and π for such a case. We have now to consider a non-ideal solution. From our present point of view its divergence from the ideal consists principally in the fact that the

molecular volume V_1 of the solvent in the pure solvent differs from its value V'_1 in the solution. Let us suppose the same thermodynamic cycle carried out as was required for the deduction of equation (1). The maximum work of transferring one mole of solvent from solvent to solution is $RT \log \pi/\pi'$. We now remove a volume V'_1 of the solvent, *i.e.* its gram-molecular volume *in* the solution, from the solution to a pure solvent state which may be called pseudo-solvent, and which differs from the ordinary solvent in that its gram-molecular volume is V'_1 in place of being V_1. This pseudo-solvent stage consists of pure solvent either under external pressure or in a state of distension,[1] depending on whether V_1 is greater or less than V'_1. The maximum osmotic work of removing one mole of solvent from the solution to this pseudo-state is PV'_1, and in writing down the final work term a negative sign has to be placed in front of this expression because it represents work done upon the system. We have now an isolated mole of solvent in a state either of compression or distension. We have therefore to alter its volume from V'_1 to V_1, and as a result of this operation the solvent will be once more in its normal state and may be added to the original vessel containing solvent without any further work being done; at the same time the cycle is completed. The above operation of altering the volume of isolated solvent from V'_1 to V_1 means work done by or upon the cohesion or intrinsic tension K. The work is $\int_{V'_1}^{V_1} K dV$.

Adding the work terms together and equating to zero, we obtain—

$$RT \log \pi/\pi' - PV_1 + \int_{V'_1}^{V_1} K dV = 0.$$

It will be observed that the fact of the solution being non-ideal, *i.e.* $V_1 \neq V'_1$, introduces the additional term involving the intrinsic tension or cohesion K. Now assuming with van der Waals that K can be written as a/V^2_1, the above relation becomes—

$$RT \log \pi/\pi' - PV'_1 + a(V_1 - V'_1)/V_1V'_1$$

whence

$$P = \frac{RT}{V'_1} \log \frac{\pi}{\pi'} + \frac{a(V_1 - V'_1)}{V_1V'^2_1} \quad . \quad . \quad . \quad (2)$$

When V_1 is greater than V'_1, *i.e.* when the *solvent* contracts on being mixed with solute, P is abnormally great. On the other hand when V_1 is less than V'_1, *i.e.* when the solvent expands on admixture, P is abnormally small. In the ideal case when the volume of the solvent is the same in both, the correction term, involving cohesion, vanishes. For this reason cohesion had not to be taken into account in the deduction of equation (1). In the above non-ideal case, marked volume changes will introduce corresponding changes in P. When contraction of the solvent occurs, the molecules are drawn together by the cohesion and we expect a loss of potential energy which will mani-

[1] Such a state has been realised experimentally by Worthington and others, *cf.* Poynting and Thomson, *Properties of Matter*, p. 122.

fest itself as evolution of heat. When heat is evolved on admixture, we would expect therefore that the osmotic pressure P would be abnormally great. In the converse case P should be abnormally small. This is in agreement with the conclusions to which Bancroft has come.

Equation (2) is the osmotic pressure equation, in terms of the solvent pressure, for non-ideal solutions. Of course the two terms on the right-hand side of the equation are interdependent. Thus, in the case in which the solvent expands on admixture (*i.e.* the case in which the final term is negative), it is evident that the molecules in the solution will be on the whole more sparsely distributed than in the case in which the volume of the solvent remained unchanged. Hence π' will be abnormally low, and therefore the first term on the right is abnormally high, and thus tends to annul the negative effect of the cohesion term. As a result of this, P remains a positive quantity. On the other hand, when contraction of the solvent occurs, the molecules are closer together, and the liquid pressure π' is greater than it would be in the ideal case. Hence the first term on the right is abnormally low under those conditions which make the second term positive. In some cases of this kind π must be equal to π', and the osmotic pressure is entirely determined by the positive final cohesion term. Now cohesion is intimately connected with surface tension, and hence in such cases there will be a connection between the surface tension and the osmotic pressure. This, according to Tinker, is the probable basis of Traube's surface tension "theory" of osmotic pressure.

Relation between the Osmotic Pressure and the Vapour Pressure.

It is well known that the vapour pressure of the solvent over the pure solvent is greater than its vapour pressure over the solution. In the case of an ideal solution, this is due to the fact that the solvent pressure in the interior of the solvent is greater than the solvent pressure inside the solution, for the greater the solvent pressure, the greater, *ceteris paribus*, the vapour pressure. Tinker assumes that they are related to one another by the Dieterici expression, *viz.* :—

Vapour pressure over pure solvent $= p_0 = \pi\ e^{-A/RT}$, and
" " " the solution $= p = \pi'\ e^{-A/RT}$.

If A is the same for pure solvent as it is for the solvent in the solution then $p_0/p = \pi/\pi'$, and the solvent pressure concept explains the fact that the vapour pressures in the two cases are different. For non-ideal solutions, the value of A cannot be regarded as the same in both, and therefore the simple relation between π and p breaks down. The A term of Dieterici is of course a measure of the cohesion K.

In the case of the ideal solution, A being the same for pure solvent and for solvent in solution, we can substitute p_0/p for π/π' and hence equation (1) gives us—

$$P = \frac{RT}{V_1} \log p_0/p$$

which is the relation already deduced in Chap. VI. of this volume.

Further, on applying external pressure to the solution, so as just to prevent osmosis, we have seen that this leads to an increase in the solvent pressure in the solution so that π' becomes identical with π. Under these conditions we would expect on the basis of the solvent pressure concept that the vapour pressures should become identical. This identity in vapour pressure at osmotic equilibrium is a thermodynamic necessity, for on transferring one mole of solvent from the solvent to the solution, *via* the vapour, the work is $RT \log p_0/p$, and this must be zero at the equilibrium point, *i.e.* $p_0 = p$. This effect of external pressure on the vapour pressure over the solution is considered from the purely thermodynamic standpoint in greater detail by Porter (*cf.* Chap. IX.).

Some Experimental Results.—So far we have regarded the solvent pressure concept of osmotic pressure as a useful working hypothesis. We have now to consider the limited experimental evidence which is available at the present time. We are again indebted to the work of Tinker (*Proc. Roy. Soc.*, **93**, A, 268, 1917), who has studied the selective properties of the copper ferrocyanide membrane, by measuring the change in the concentration of a solution of sucrose in water which takes place when the dried colloid is immersed in solutions of various strengths. As a result of adding the colloid it is found that the solutions become stronger, *i.e.* the ratio of sucrose to water increases owing to the fact that the water and not the sugar is taken up selectively, by adsorption by the ferrocyanide. *The amount of adsorbed moisture taken up by the colloid decreases as the strength of the solution with respect to sucrose increases.* This is a fundamental observation for it indicates that the membrane takes up more moisture from pure water than it does from an aqueous solution, so that, if pure water be on one side of the membrane and a solution on the other, the concentration of water in the membrane on the pure water side is greater than its concentration on the solution side, with the result that there is a tendency for water to flow *into* the solution, *i.e.* osmosis occurs. To prevent osmosis a hydrostatic pressure must be placed upon the solution. Provided the pressure is applied to the solution only and not to the pure solvent as well, the application of the pressure increases the amount of moisture taken up by that part of the colloid in contact with the solution; and when a hydrostatic pressure equal to the osmotic pressure is placed on the solution the moisture pressure and its concentration become uniform throughout the membrane, osmotic flow then ceasing. Tinker further mentions that some unpublished work by A. J. Brown and himself indicates that if the pressure be placed upon the membrane as well as upon the solution the amount of water taken up by the colloid does not increase. Adsorption is evidently the factor which determines the suitability of a given membrane as regards semipermeability; adsorption is not the cause of osmotic pressure.

Intrinsic Pressure and Solvent Pressure.—We must be careful to distinguish the term solvent pressure from the internal, intrinsic or cohesion pressure or tension already discussed in Chap. III., Vol. II. This

cohesive force when reckoned per unit area in the interior of a liquid is denoted by the symbol K and has already entered into our considerations. It has its origin in molecular attractions, and manifests itself as a backward pull exerted upon the molecules when they approach the surface. It is measured by the term a/V^2 in van der Waals' equation, or by the term A in Dieterici's. On the other hand, the solvent pressure π is a purely kinetic bombardment pressure existing in the interior of the liquid and governed by the relation $\pi(V - b) = RT$. The justification of writing the term RT rests upon the applicability of the principle of equipartition of kinetic energy between the individuals in a system at a given temperature, the energy being of the translational kind. As already stated the internal pressure or tension, although present throughout the entire liquid cancels itself out in the interior, and the molecules are just as free to move as gas molecules are, but, of course, in a very much smaller available or free space.

Binary Mixture consisting of Two Liquids. Relation between the Partial and Total Liquid Pressures in Terms of the Relative Molecular Concentrations of the Two Components.

A discussion of this problem is necessary to the better understanding of the osmotic behaviour of a solution. The treatment here given is due to Tinker.

Let X and Y be the two components of the liquid mixture, and let N molecules of X be mixed with n molecules of Y. Also let,

π_1 = liquid pressure of pure X. Incompressible volume of X = b_1
π_2 = liquid pressure of pure Y. Incompressible volume of Y = b_2
π'_1 and π'_2 are the partial liquid pressures of X and Y in the mixture.
V_1 and V_2 are the molecular volumes of pure X and pure Y respectively.
V'_1 and V'_2 are the molecular volumes of X and Y in the mixture.

In general, V'_1 and V'_2 will be different from V_1 and V_2. The molecular volume of each constituent alters on mixing in such a way that $V'_1 - b_1$ becomes equal to $V'_2 - b_2$, each of these terms being identical, because they represent the mean free space F per molecule of either kind in the mixture. The molecules in the mixture arrange themselves so as to be distributed evenly throughout, this state of affairs representing the equilibrium condition. In order to realise the condition that $V_1 = V'_1$ and $V_2 = V'_2$ (*i.e.* the condition that the molecular volumes of both liquids remain unchanged on mixing), we must have $V_1 - b_1 = V_2 - b_2$ initially. Since this last equality would happen only rarely, it would be equally rare to find $V_1 = V'_1$ and $V_2 = V'_2$ simultaneously. But it can be shown (*vide infra*) that for dilute solutions (*i.e.* one of the constituents, which we can call the solvent, being in large excess) we may have $V'_1 = V_1$ (the molecular volume of the solvent may be the same before and after mixing), although at the same time V'_2 may be very different from V_2 (*i.e.* the molecular volume of the *solute* may have changed considerably). Let us consider, however, the general case in which V_1 and V_2 differ respectively from V'_1 and V'_2.

Consider, first, the partial liquid pressure π'_1 of the component X in the mixture. Before the N molecules of X are mixed with the n molecules of Y, the liquid pressure π_1 of the pure X is given by—

$$\pi_1 = \frac{NRT}{N(V_1 - b_1)} \quad . \quad . \quad . \quad . \quad (3)$$

where the constant R refers to one gram-molecule of X. The term $N(V_1 - b_1)$ is the free space allotted to N molecules. Now add the n molecules of Y. We then have—
volume of the free space in the mixture =

$$N(V'_1 - b_1) + n(V'_2 - b_2).$$

Hence the partial liquid pressure π'_1 of the component X in the mixture is given by—

$$\pi'_1 = \frac{NRT}{N(V'_1 - b_1) + n(V'_2 - b_2)} = \frac{NRT}{(N + n)(V'_1 - b_1)} \quad . \quad (4)$$

since $V'_1 - b_1 = V'_2 - b_2 = F$, the mean free space per molecule of either kind in the mixture. Combining equations (3) and (4) we obtain—

$$\frac{\pi_1}{\pi'_1} = \frac{N + n}{N} \cdot \frac{V'_1 - b_1}{V_1 - b_1} = \frac{N + n}{N} \cdot \frac{F}{V_1 - b_1} \quad . \quad . \quad (5)$$

This relation should hold good whether there has been any volume change on mixing or not. (When we speak of no volume change taking place on mixing we mean that the total volume is exactly the sum of the separate volumes of the components.)

Similarly, for component Y—

$$\frac{\pi_2}{\pi'_2} = \frac{N + n}{n} \cdot \frac{V'_2 - b_2}{V_2 - b_2} = \frac{N + n}{n} \cdot \frac{F}{V_2 - b_2}.$$

Relation between the Osmotic Pressure of a Solution and the Relative Molecular Concentrations of the Solvent and Solute.

Let us now think of a solution in which X is the solvent and Y the solute. N is now much greater than n. From equation (5) it follows that the ratio of the solvent pressures in pure solvent and in the solution respectively would be equal to $(N + n)/N$, provided $V'_1 - b_1 = V_1 - b_1$, that is, provided the solvent had the same molecular volume in the pure state and in the solution. This statement has already been used as a definition of an *ideal* solution. Hence for an ideal solution we can write—

$$\pi/\pi' = (N + n)/N$$

where π is the liquid pressure of the pure solvent.

Now for such a solution it has already been shown equation (1a) that the osmotic pressure P is given approximately by—

$$P = \frac{RT}{V_1} \cdot \frac{\pi - \pi'}{\pi'}.$$

Combining this with the relation just obtained, we find—

$$P = \frac{RT}{V_1} \cdot \frac{n}{N}.$$

The product V_1N is the actual volume of the solvent which contains N molecules, whilst n is the number of molecules of solute present in the solution which contains this amount of solvent. We can therefore write n/NV_1 as c, where c is the concentration of the solute expressed as number of molecules in a given volume (actually volume of solvent, not that of solution, though in a very dilute solution they will be almost identical quantities).

Hence $$P = RTc$$

which is the ordinary van 't Hoff relation for the osmotic pressure of a dilute solution. This relation may therefore be deduced, as a first approximation on the basis of the liquid pressure concept of osmotic pressure in the limiting case of an ideal solution.

The Non-Ideal Solution.

In general the solvent itself will undergo a certain amount of volume change (compression or extension), when the solute is added. In general, therefore, V_1 and V'_1 are not identical. We have now to see how far such a change in the molecular volume of the solvent affects the simple van 't Hoff relation just obtained.

The accurate relation is given by equation (5). We have to examine the magnitude of the error involved in putting—

$$(V_1 - b_1) \text{ equal to } (V'_1 - b_1)$$

in the case of actual solutions. The following mode of procedure is suggested by Tinker. Suppose that on mixing, the total volume increases by an amount ne (where e can be regarded as the expansion of solution per molecule of solute added). We then have—

Total volume of solution $= NV_1 + nV_2 + ne.$
Total free space in solution $= N(V_1 - b_1) + n(V_2 - b_2) + ne.$
That is, $(N + n)F = N(V_1 - b_1) + n(V_2 - b_2 + e)$
$$= (N + n)(V_1 - b_1) - n\{(V_1 - b_1) - (V_2 - b_2 + e)\}$$

Dividing throughout by $(N + n)(V_1 - b_1)$ we obtain—

$$\frac{F}{V_1 - b_1} = 1 - \frac{n}{N + n}\left(1 - \frac{(V_2 - b_2 + e)}{V_1 - b_1}\right) \quad . \quad . \quad (6)$$

But, $$\frac{\pi}{\pi'} = \frac{N + n}{N} \cdot \frac{V'_1 - b_1}{V_1 - b_1} = \frac{N + n}{N} \cdot \frac{F}{V_1 - b_1}.$$

Hence, $$\frac{\pi}{\pi'} = \frac{N + n}{N} - \frac{n}{N}\left(1 - \frac{V_2 - b_2 + e}{V_1 - b_1}\right) \quad . \quad . \quad (6a)$$

The error in writing $\pi/\pi' = (N + n)/N$ is only absolutely zero when

$$V_2 - b_2 + e = V_1 - b_1.$$

The error is not appreciable, however, so long as n is small compared with N, that is, so long as the solution is dilute. Hence, van't Hoff's expression will apply to a very dilute solution even though this is not strictly ideal. The order of magnitude may be estimated in the following way. Consider a decinormal solution in water, and as an extreme case let $(V_2 - b_2 + e) = 10(V_1 - b_1)$. We then have $n/N = 1/550$ and $(N + n)/N =$ unity approx. Hence,

$$\frac{n}{N}\left(1 - \frac{(V_2 - b_2 + e)}{V_1 - b_1}\right) = -\frac{1}{60} \text{ approx.}$$

That is, the error of writing $\pi/\pi' = (N + n)/N$ is 1/60 on unity or less than 2 per cent.

It is evident that the error is mainly determined by the number of solute molecules added to the solvent. If not many are added, *i.e.* if the solution is very dilute, their influence on the mean free space F in the mixture is swamped by the influence of the solvent. In such a case we can write approximately $V_1 - b_1 = V'_1 - b_1$. But in all cases it is accurate to write $(V'_1 - b_1) = (V'_2 - b_2)$, since each of these terms is simply F. Hence in the particular case examined we have—

$$V'_2 - b_2 = V'_1 - b_1 = V_1 - b_1.$$

That is, in a very dilute solution the average free space allotted to each *solute* molecule is practically identical with the free space per molecule of the pure *solvent*. It follows therefore that the molecular volume V_2 of the pure undissolved solute may be altered very much by dissolution, for its new value in the solution, *viz.* V'_2, is now equal to $(V_1 + b_2 - b_1)$. *Under conditions therefore in which the molecular volume of the solvent remains practically unchanged, the molecular volume of the solute may (and in general will) be altered considerably.*

The Conditions under which the Process of Mixing Involves no Change in the Volume of the Components, i.e. *the resulting volume is exactly equal to the sum of the separate volumes.*

Using the notation of the preceding section, we have to find the conditions under which $ne = 0$.

The mean free space per molecule of either kind in the solution has been denoted by the symbol F which is equivalent to $V'_1 - b_1$. Hence equation (6) previously obtained may be written thus :—

$$\frac{V'_1 - b_1}{V_1 - b_1} = 1 - \frac{n}{N + n}\left(1 - \frac{(V_2 - b_2 + e)}{V_1 - b_1}\right).$$

It follows therefore that

$$\frac{V_1 - V'_1}{V_1 - b_1} = \frac{n}{N + n}\left\{\frac{(V_1 - b_1) - (V_2 - b_2 + e)}{V_1 - b_1}\right\}.$$

or

$$(N + n)(V_1 - V'_1) = n\left((V_1 - b_1) - (V_2 - b_2 + e)\right) \quad . \quad (7)$$

whence the total expansion on mixing, namely ne, is given by—

$$ne = n((V_1 - b_1) - (V_2 - b_2)) - (N + n)(V_1 - V'_1) \quad . \quad (7a)$$

There are therefore *two* cases in which $ne = 0$, *i.e.* in which there is no volume change on mixing.

First, $ne = 0$ when—

$$\left.\begin{aligned} V_1 - b_1 &= V_2 - b_2 \\ \text{and} \quad V_1 &= V'_1 \end{aligned}\right\} \text{ simultaneously.}$$

This condition, it will be observed, contains the further condition that $V_2 = V'_2$, *i.e.* the molecular volume of the *solute* is unaltered on mixing. This may be shown as follows. The mean free space F in the solution $= V'_1 - b_1 = V'_2 - b_2$. The condition considered is however that $V_1 - b_1 = V_2 - b_2$, and also $V_1 = V'_1$.

Hence $$V'_1 - b_1 = V_2 - b_2 = V'_2 - b_2.$$

Hence $V_2 = V'_2$. The condition that the free space per molecule shall be the same in the separate substances is very unlikely to occur in practice; hence this first condition for absence of change in volume on mixing will be unlikely.

Secondly, $ne = 0$ when

$$(N + n)(V_1 - V'_1) = n((V_1 - b_1) - (V_2 - b_2))$$

or when $$V_1 - V'_1 = \frac{n}{N + n}\left\{(V_1 - b_1) - (V_2 - b_2)\right\}.$$

That is, there will be no total volume change when the actual alteration in V_1 is such as to be identical with $n/N + n$ times the difference between the free space in the two separate constituents.

The first point to notice about this condition is that a change of V_1 to the value V'_1 does not necessarily involve a change in the total volume of the mixture. We are considering a non-ideal solution—non-ideal, because we allow the molecular volume of the solvent to alter. Yet the total volume can remain unchanged under these conditions. The absence of total volume change on mixing is therefore not necessarily a criterion of an ideal solution, though at first sight it might have appeared to be so. The criterion for ideal behaviour is constancy in the value of the molecular volume of the solvent, *i.e.* it must be the same in the pure state and in the solution respectively. It is only then that equation (1) is true.

The next point to observe in connection with this condition for absence of total volume change on mixing is that with most pairs of substances there will be *one* proportion (*i.e.* one value of $n/(N + n)$) which will satisfy the condition that $ne = 0$. This follows from the fact that the term $n/(N + n)$ controls to a large extent the value of the expression on the right-hand side.

Membrane Structure in Relation to Semi-permeability.

Experiment has shown that membranes consist of collections of very small particles of colloidal precipitate. The following table due to

Tinker (*Proc. Roy. Soc.*, **92**, A, 357 (1916)) gives the average size of particle for different substances :—

Membrane.	Diameter of Particle
Copper ferrocyanide . .	0·1 to 0·4μ
„ silicate . . .	0·2 „ 0·5μ
Lead silicate . . .	0·6 „ 0·8μ
Peptone tannate . .	0·5 „ 1·0μ
Barium sulphate . .	—
Silver chloride . . .	coagulate into large particles 3 to 4μ in diameter.

Each of these visible particles is itself an aggregate of smaller colloidal particles. There are therefore two sorts of pores, those between the aggregates and those penetrating each aggregate. No sharp distinction can be drawn between them. Tinker estimates that the smaller pores possess a diameter of about 10$\mu\mu$, the larger pores a diameter of about 50 $\mu\mu$. The best semipermeable membranes are those with the smallest pores, but this cannot be the only criterion, for osmotic effects have been exhibited by membranes containing pores which are so many times greater than the diameter of a molecule that it is impossible to regard the membrane as offering any permanent obstacle to the diffusion of the solute on this ground alone. Thus Bartell (*Journ. Phys. Chem.*, **16**, 318 (1912)) has shown that osmotic effects become noticeable even with a pore diameter of 900$\mu\mu$, and are quite appreciable with a pore diameter of 180$\mu\mu$. The semipermeability is evidently a question of capillary selective adsorption of the solvent. If the solute be preferentially adsorbed the membrane is no longer semipermeable in the ordinary sense. The capillary effect may be modified by electrical effects. Thus in the case of electrolytes Bartell and Hocker (*Journ. Amer. Chem. Soc.*, **38**, 1029 (1916)) have shown that in certain instances it is possible to realise a negative osmosis, *i.e.* diffusion of the liquid from strong concentration to weak. "The explanation which seems most reasonable is that the osmose is due to the passage of a charged liquid layer along the capillary tubes of the membrane under the driving force of a difference of potential which acts as though it were set up between the two faces of the membrane. The charge of the movable liquid layer is determined by the charge which the porcelain [the membrane employed by Bartell] assumes when immersed in water, but this charge may be altered by selective adsorption of ions when the membrane is brought into contact with solutions of electrolytes."

These capillary and electrocapillary views, it must be understood, refer only to the possible mechanism of semipermeability of membranes. This is quite distinct from the origin of osmotic pressure itself, which has been attributed to a difference between the value of the solvent pressure throughout the body of the pure solvent, and the value of the solvent pressure throughout the body of the solution.

Stress must be laid on the fact that the views expressed in the foregoing sections regarding the origin of osmotic pressure are at the present

time to be regarded as tentative. They represent the treatment of the subject to a large extent by a single investigator. They have been discussed at some length, however, because in the present writer's opinion they represent the most satisfactory treatment of the mechanism of osmotic pressure available at the present time.

In the further consideration of the properties of solutions, given in the present and in the succeeding chapter, it is not necessary to make any assumptions regarding the ultimate mechanism of osmotic pressure. The experimental fact is that dilute solutions exhibit a close quantitative *analogy* to the behaviour of gases, in that the gas law is more or less obeyed. According as this analogy holds or not we shall speak of "normal" and "abnormal" behaviour on the part of the solute.

MODERN THEORY OF DILUTE SOLUTIONS OF ELECTROLYTES.

As already pointed out in Vol. I. (Chap. V.) the outstanding problem in connection with dilute solutions is that known as the anomaly of strong electrolytes, *viz.* the fact that such substances do not obey the law of mass action in respect of the equilibrium between the undissociated molecules and the ions, the concentrations of these constituents being determined by the conductivity method.

The investigations of this problem from the standpoint of thermodynamics, which have been pursued for a considerable number of years, have greatly extended our knowledge of the behaviour of such solutions. This advance, as will be inferred from the references given below, has been made chiefly by the American School of Physical Chemistry.

Broadly speaking, two lines of approach have been followed. In the first, the idea of actual *concentrations* of ions and undissociated molecules is regarded as the fundamental factor in determining the equilibrium between the different species. As a measure of such concentrations the conductivity method is regarded as reasonably correct. Since the law of mass action, expressed in such concentration terms, is known not to apply—which means, as the thermodynamic deduction of the law implies, that in the case of strong electrolytes the osmotic pressure either of the molecules or of the ions (or of both) does not obey the gas law—attempts have been made to find a modified law of mass action which would reproduce the actual behaviour of the molecular and ionic species considered. That is, the osmotic pressure of a species is no longer regarded as simply proportional to the concentration. Such modifications have to be expressed by means of empirical coefficients, *e.g.* Storch's equation. In this mode of treatment, which is illustrated below by a résumé of Bates' paper, it is necessary, in order to deal with actual numerical values to assume the validity of the conductivity method.

In the second mode of treatment, not only is the conductivity method discarded, but the idea that actual concentration of ions and molecules (which the conductivity method, if valid, would undoubtedly give) is the determining factor for active mass is no longer regarded as true. In place of this, a new and more subtle concept is introduced,

namely, *effective concentration* or *activity*. These terms will be defined in their proper place when we are dealing with the work of G. N. Lewis, A. A. Noyes, MacInnes and others. This method of attack correlates the various thermodynamic relationships which we have already dealt with in connection with solutions in general, *viz.* the lowering of the freezing point, lowering of vapour pressure, rise of boiling point, electromotive force of concentration cells, and the law of mass action itself.

This method is virtually a new way of expressing the law of mass action, in which a wider significance is given to the term active mass than is given by identifying it with mere concentration. This new idea which has been arrived at from the point of view of thermodynamics, in the first place by G. N. Lewis, finds its counterpart or complement in molecular-mechanical terms through the introduction by the writer of the quantum hypothesis into ordinary or thermal chemical reactions. A tentative suggestion in this connection is made towards the end of this chapter.

We now proceed to take up in a little more detail the two lines of investigation, or modes of treatment referred to above. In doing so, it is to be clearly understood that the sections headed—Degree of Dissociation and the numerical value of the equivalent conductivity at infinite dilution; Osmotic Pressure and concentration in solutions of electrolytes and the calculation of the degree of ionisation; Reaction Velocity in relation to the osmotic pressure of ions and molecules; Ionisation in formic acid solutions—these sections belong to the first mode of treatment of strong electrolytes, whilst the remaining sections are illustrative of the second method.

The Degree of Dissociation and the Numerical Value of the Equivalent Conductivity at Infinite Dilution.

An interesting relation has been pointed out by G. N. Lewis (*Journ. Amer. Chem. Soc.*, **34**, 1631, (1912)) between the magnitude of Λ_∞ and the values of Λ_v/Λ_∞ at a given concentration, for a number of acids, bases, and salts of the uni-univalent type. The point is illustrated in the following table in which the electrolytes are grouped according to the value of Λ_∞. The particular concentration chosen for comparison is decinormal, and the value of Λ_v/Λ_∞ holds for that concentration, Temperature 18° C.

Number of Electrolytes Examined.	Λ_∞.	Λ_v/Λ_∞.
2	390—370	0·923
2	220—200	0·895
12	140—130	0·860
4	130—120	0·831
10	120—100	0·833
5	100— 90	0·819
2	80— 70	0·779
3	70— 60	0·761

It is evident that the values of Λ_v/Λ_∞ diminish, *i.e.* the degree of ionisation apparently diminishes with decreasing Λ_∞. "There is nothing in the present theory of electrolytic dissociation which would enable us to predict this result, and the question arises as to whether the variation in Λ_v/Λ_∞ means a real variation in the degree of dissociation." The highest values of Λ_v/Λ_∞ are those of hydrochloric and nitric acids, *viz.* 0·925 and 0·921. Lewis deals with this question from the standpoint of the transport numbers of the various ions, which, according to many measurements, show a variation with the concentration of the electrolyte. The conclusion arrived at is that HCl has the same degree of dissociation as KCl, *i.e.* the simple conductivity expression is not quantitatively correct owing to the change of mobility of the ions with concentration, the change being in the sense that with *increase* in concentration of the salt the mobility *increases*. This effect, if it exists, is thus in the opposite sense to that due to viscosity.

The conclusion is legitimate, provided that the true transport numbers really alter with concentration. This, however, has been called in question in view of the newer results obtained by means of the reference substance method of determining transference numbers.

In connection with Lewis's suggestion regarding a possible increase in the mobility of an ion as the concentration increases, it is worth while to draw attention to some striking results obtained many years ago by Arrhenius on the rate of diffusion of HCl into NaCl solutions of different concentrations, in which it was shown that the more concentrated the salt solution the greater the diffusion coefficient of the HCl into the salt solution. This is illustrated by the following data. A solution 1·04 molar with respect to HCl and at the same time 0·1 molar with respect to NaCl diffused into a column of liquid 0·1 molar with respect to NaCl. The diffusion coefficient of the acid, *i.e.* the hydrogen ion, was 2·50.

A second solution, likewise 1·04 molar with respect to HCl and simultaneously 0·67 molar with respect to NaCl, diffused into a solution of NaCl, 0·67 molar. The diffusion coefficient of the hydrogen ion was now 3·51. When diffusion took place into pure water the diffusion coefficient was 2·09. Similar results were obtained with NaOH.[1] The presence of electrolyte appears to increase the rate of diffusion of the ion. The change in the diffusion coefficient here observed is large, much larger than the effect considered above in dealing with equivalent conductivity. It is remarkable, however, that no adequate explanation of the behaviour observed by Arrhenius has as yet been suggested.

[1] In the case of non-electrolytes, *e.g.* sucrose, the diffusion coefficient *falls* with increase in the concentration, so that the increase in diffusion observed by Arrhenius is connected with the presence of ions (*cf.* Arrhenius, *Theories of Chemistry*, p. 189 *seq.* *Cf.* also Oholm's results quoted in Chap. IX., Vol. I.).

Osmotic Pressure and Concentration in Solutions of Electrolytes and the Calculation of the Degree of Ionisation.

This subject is dealt with by S. J. Bates (*Journ. Amer. Chem. Soc.*, **37**, 1421 (1915)). In the discussion given below Bates' own words have been employed extensively.

The divergence of strong electrolytes from Ostwald's dilution law may be due to abnormality in the behaviour of the ions, to abnormality of the undissociated molecule, or to abnormality in both. This so-called anomalous behaviour may be simply expressed thus : *for one or for both of these molecular species van 't Hoff's law* $\pi V = RT$ *does not hold, for if all of the molecular species entering into an equilibrium obey this law, the law of mass action is a thermodynamic necessity* (*cf.* Washburn, *Journ. Amer. Chem. Soc.*, **32**, 485, (1910)). The symbol π denotes osmotic pressure on Bates' nomenclature. (It is not to be confused with the π of the earlier part of this chapter.) We have already seen in Chap. V. that the gas law is assumed for all the constituents taking part in the reaction in order to deduce the law of mass action for a gaseous system. The same must be true of the osmotic pressures of all the reacting constituents in a solution in order to deduce the law of mass action in this case also.

The object of the present considerations is to develop and apply methods for determining the numerical relation which holds, in place of that given by van 't Hoff's law, between the osmotic pressure of the ions and their concentration, and the similar relation for the undissociated molecules, with the further object of studying each effect separately as far as possible in the case of strong electrolytes, *i.e.* systems which do not obey the law of mass action. *The calculations will be based upon the assumption that the degree of ionisation may be determined from conductivity data, i.e.* that $\gamma = \Lambda \,.\, \eta/\Lambda_\infty\eta_0$.

Principle of the Method Employed by Bates.

If it be assumed that, in a solution of a di-ionic electrolyte, *e.g.* KCl, the osmotic pressure due to one of the ions is equal to that due to the other, then thermodynamics yields for equilibrium in solution the rigorous relation—

$$2d\pi_i/C_i - d\pi_u/C_u = 0 \quad . \quad . \quad . \quad . \quad (1)$$

(*cf.* Washburn, *loc. cit.*), where π_i and π_u are the osmotic pressures due to the ions at the concentration C_i, and the undissociated molecules at the concentration C_u respectively. It follows at the same time that—

$$\pi = 2\pi_i + \pi_u \quad . \quad . \quad . \quad . \quad . \quad (2)$$

that is, the total osmotic pressure π of the solution is the sum of two effects, one, the osmotic pressure of the ions, the other, that of the undissociated molecules. If now C_i and C_u are calculated from conductivity data, and if the total osmotic pressure of the solution be known

(either from direct measurements or from freezing point determinations), it is possible to determine, for any concentration interval for which data are available, the relation between π_i and C_i and the relation between π_u and C_u; for there are two equations and two unknown quantities, π_i and π_u. The first point therefore is to calculate the total osmotic pressure π from freezing point data.

Calculation of Total Osmotic Pressure from Freezing Point Data.—From the lowering of freezing point, Δt_F, the total osmotic pressure may be readily and accurately calculated by means of the equation (Washburn, *loc. cit.*)—

$$\pi = 12{\cdot}06(\Delta t_F - 1{\cdot}78 \times 10^{-3}\Delta t_F^2 - 2{\cdot}5 \times 10^{-6}\Delta t_F^3 \quad . \quad (3)$$

It is convenient to compare osmotic pressures at 0° C., and Bates shows that the temperature correction to be applied—which is a small one—causes the previous equation to take the form—

$$\pi = 12{\cdot}06(1 + 0{\cdot}00188\Delta t_F)\Delta t_F \quad . \quad . \quad . \quad (4)$$

This equation gives within a few hundredths of 1 per cent. the total osmotic pressure at 0° C of solutions as concentrated as 0·2 N, and, within 0·2 to 0·3 per cent. the osmotic pressure of solutions up to 0·5 N. This correct mode of calculating osmotic pressure from freezing point data must be borne in mind, for, as will be shown, the usual method of calculating osmotic pressure from the freezing point—by using the lowering of freezing point to calculate the van 't Hoff factor i and then calculating π by means of the empirical relation $\pi V = iRT$—is erroneous in this respect, that it assumes implicitly that the ions *and* the undissociated molecules obey van 't Hoff's law (gas law). We know that this cannot be true for *both* sorts of individuals simultaneously (and may not be true for either) as this assumption would necessitate the applicability of the law of mass action for the dissociation of any electrolyte.

The above argument may be restated in the following way. Suppose that one mole of KCl is dissolved in V liters of solution. Owing to dissociation there are $(1 - x)$ undissociated moles, x cations and x anions, the total number of individuals being $(1 + x)$, where $(1 + x)$ is identical with van 't Hoff's factor i. Now suppose that the ions and the undissociated molecules obey the gas law. If π_i is the osmotic pressure of either of the ions and π_u the osmotic pressure of the molecules it follows on the above assumption that—

$$\pi_i V = RTx \text{ for the cations}$$
$$\pi_i V = RTx \text{ for the anions}$$
$$\pi_u V = RT(1 - x) \text{ for the undissociated molecules.}$$

Hence $2\pi_i V + \pi_u V = 2xRT + (1 - x)RT$,

or $(2\pi_i + \pi)V = RT(1 + x) = iRT$.

But, as already pointed out, it is necessarily and fundamentally true that the total observed osmotic pressure π is given by—

$$\pi = 2\pi_i + \pi_u$$

and therefore, $\pi V = iRT$

which is the relation *usually* taken to be true in calculating i or x (and therefore indirectly π_i and π) from freezing point data. The above relation is incorrect in that it assumes that the ions and simultaneously the undissociated molecules obey the gas law, which we know cannot be true, since ionisation of a strong electrolyte does not obey the law of mass action. (A different mode of demonstrating this very important conclusion due to Bates will be given later.) This criticism applies to the calculation first carried out by Arrhenius and referred to in Vol. I., Chap. V. It may be pointed out, however, that the dissociation calculated from the freezing point data by the above (erroneous) method agrees fairly well with that obtained from conductivity data. This as will be shown later is due to the fact that the deviation of the ions from the gas law in one direction is nearly compensated by the deviation of the molecules in the other.

Solution of the Equations.—The object before us is to calculate, in the case of a strong electrolyte such as KCl, the osmotic pressure exerted by the undissociated molecules and by the ions (as distinct from the molecules) in order to see whether one sort or both sorts deviate from van 't Hoff's law, and thereby cause the law of mass action to be inapplicable. It is assumed that the concentration of the ions C_i and of the undissociated molecules C_u can be obtained accurately from the conductivity expression, the symbol γ being used to denote the ionisation coefficient determined by this method. When the terms C_i and C_u occur, it is to be understood that they are determined directly by conductivity. At the same time we require to know the total osmotic pressure π of the solution and this is to be understood as directly obtainable from the freezing point data by means of equation (4).

Equation (1) may be written in the form—

$$2(1 - \gamma)d\pi_i - \gamma \cdot d\pi_u = 0 \quad . \quad . \quad . \quad (5)$$

By differentiating equation (2), multiplying through by γ and adding the result to (5), we obtain :—

$$d\pi_i = (\gamma/2)d\pi \quad . \quad . \quad . \quad . \quad (6)$$

From the differential calculus we have—

$$d(\pi/C_i) = \frac{C_i d\pi - \pi dC_i}{C^2_i} \quad . \quad . \quad . \quad . \quad (7)$$

and therefore,

$$\frac{d\pi}{dC_i} = \frac{\pi}{C_i} + \frac{d(\pi/C_i)}{d \log C_i} \quad . \quad . \quad . \quad . \quad (7a)$$

and from (6)

$$\frac{d\pi_i}{dC_i} = \frac{\gamma}{2}\frac{d\pi}{dC_i} = \frac{1}{2}\left[\frac{\pi}{C} + \frac{\gamma}{2{\cdot}303} \cdot \frac{d(\pi/C_i)}{d \log_{10} C_i}\right] \quad . \quad . \quad (8)$$

This expression can be used to determine $(d\pi_i/dC_i)$, *i.e.* the rate of change of the osmotic pressure of the ions with their concentration. The ratio π/C in equation (8) can be got directly from freezing point

data, for π is the total osmotic pressure of the solution and C is the total concentration of the salt. The value of $\frac{d(\pi/C_i)}{d \log C_i}$ may be obtained graphically or algebraically. Having thus evaluated the right-hand side of equation (8) we obtain values of $(d\pi_i/dC_i)$ at a series of dilutions. From this by integration—as will be referred to later—we can obtain values of π_i/C_i, *i.e.* the actual osmotic pressure of an ion divided by the concentration of the ion. In order to obtain similar ratios for the undissociated molecules, a procedure similar to the above could be employed. In practice, however, it is more convenient to use a different method.

By eliminating K, C_i, and C_u from Storch's equation,[1] *viz.* $C_i^{n_0}/C_u = K$, from the differential equation obtained derived from this (C_i and C_v being taken as the variables), and from equation (1) we obtain the relation—

$$\frac{d\pi_u}{dC_u} = \frac{2}{n_0} \cdot \frac{d\pi_i}{dC_i} \quad . \quad . \quad . \quad . \quad (9)$$

That is, having determined $(d\pi_i/dC_i)$ and values for n_0 (already calculated by Bates, *Journ. Amer. Chem. Soc.*, **35**, 519, (1913)) over a given concentration range, it is possible to calculate $(d\pi_u/dC_u)$, and hence by integration to determine the osmotic pressure of the undissociated molecules as a function of their concentration.

Experimental Illustration. Potassium Chloride in Aqueous Solution.—The table which follows contains details of the above calculation applied to KCl. In the first column is given the concentration of the salt in equivalents per liter (C); in the second, the corresponding values of the lowering of freezing point, Δt_F, divided by the concentration n' of the total salt expressed as moles per 1000 grams of water. These data are due to Flügel (*Zeitsch. phys. Chem.*, **79**, 585, (1912)), Jahn (*ibid.*, **50**, 129, (1904); *ibid.*, **59**, 31, (1907)); Loomis (*Wied. Ann.*, **57**, 495 (1896)); Barnes (*Trans. Nova Scot. Inst. Sci.*, **10**, 153); and to Noyes and Falk (*Journ. Amer. Chem. Soc.*, **32**, 1011, (1910)). From known density determinations, values of $\Delta t_F/C$ were obtained from the values of $\Delta t_F/n'$, and then, by the aid of equation (4), the values of $\pi/C \div RT$ were calculated. These are given in column III.

By dividing the data of column III. by the degrees of dissociation γ* the values of $(\pi/C_i) \div RT$ were obtained (column IV.). These were then plotted against values of log C_i, and the tangents $\frac{d(\pi/C_i) \div RT}{d \log C_i}$, given in column V., were determined from the curve.

Values of $\left(\frac{d\pi_i}{dC_i}\right) \div RT$ were then calculated by means of equation (8)

[1] This equation is a purely empirical one which applies to the dissociation of a strong electrolyte, such as KCl. n_0 is not 2 as in the case of the Ostwald dilution expression.

* The conductivity data refer to 18° C., but as Bates points out, the error due to the temperature change (down to 0° C.) is smaller than the experimental error itself.

and are given in column VI. The figures of the Storch coefficient n_0 (column VII.) were calculated from conductivity data, and were used to compute the values of $(d\pi_u/dC_u) \div RT$, by means of equation (9). These values are given in column VIII. In order to integrate the coefficients in columns VI. and VIII., values of log $(1 - (d\pi_i/dC_i) \div RT)$ were plotted against values of log C_i, and those of log $((d\pi_u/dC_u) \div RT - 1)$ against values of log C_u. The curves are straight lines. From the first curve it was found that—

$$(d\pi_i/dC_i) \div RT = 1 - 0{\cdot}0552\ C_i^{0{\cdot}207}$$

whence by integration—

$$(\pi_i/C_i) \div RT = 1 - 0{\cdot}0457\ C_i^{0{\cdot}207}. \quad . \quad . \quad (13)$$

Similarly it was found that

$$(\pi_u/C_u) \div RT = 1 + 0{\cdot}464\ C_u^{0{\cdot}0632} \quad . \quad . \quad (13a)$$

From these equations the values of $(\pi_i/C_i) \div RT$ and of $(\pi_u/C_u) \div RT$ were calculated ; these are given in columns IX. and X. By adding the osmotic pressure of the ions and the molecules and dividing the result by RT, a series of values was obtained which agreed very closely with those of column III., indicating that the equations 13 and 13a express the data with accuracy.

CALCULATION OF THE OSMOTIC PRESSURE OF THE IONS AND OF THE UNDISSOCIATED MOLECULES IN SOLUTIONS OF POTASSIUM CHLORIDE FROM FREEZING POINT AND CONDUCTING DATA.

Col. I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
C_i	$\Delta t_F/m'$.	$\pi/C \div RT$.	$\pi/C_i \div RT$	$\frac{d(\pi/C_i \div RT)}{d \log C_i}$.	$\frac{d\pi_i/dC_i}{RT}$.	(Storch's Coeff.) n_0.	$d\pi_u/dC_u \div RT$.	$\pi_i/C_i \div RT$.	$\pi_u/C_u \div RT$.
0·001	3·662	1·9708	2·0052	0·0055	0·9866	1·580	1·249	0·9892	1·232
0·002	3·638	1·9578	2·0084	0·0216	0·9835	1·558	1·262	0·9876	1·248
0·005	3·612	1·9439	2·0246	0·0548	0·9833	1·525	1·289	0·9849	1·271
0·01	3·584	1·9293	2·0420	0·0702	0·9791	1·500	1·305	0·9826	1·289
0·02	3·553	1·9131	2·0672	0·100	0·9766	1·474	1·325	0·9800	1·308
0·05	3·498	1·8852	2·1120	0·143	0·9703	1·438	1·350	0·9760	1·334
0·1	3·457	1·8666	2·1626	0·182	0·9673	1·407	1·375	0·9725	1·354
0·2	3·394	1·8380	2·2149	0·231	0·9605	1·376	1·396	0·9685	1·375
0·3	3·359	1·8251	2·2590	0·260	0·9581	1·357	1·412	0·9658	1·386
0·4	3·334	1·8173	2·2915	0·280	0·9568	1·344	1·424	0·9640	1·396
0·5	3·314	1·8130	2·3171	0·291	0·9557	1·335	1·432	0·9624	1·403

In addition to the data for KCl, Bates has likewise recorded the less complete data for a number of other salts, NaCl, $NaClO_3$, LiCl, $NaNO_3$, KNO_3, $CsNO_3$, $CuSO_4$, and $MgSO_4$. The general conclusion to be drawn is, that whilst solutions of salts become more normal in behaviour as the dilution increases, yet, even in solutions as dilute as 0·001 N, *neither the ions nor the undissociated molecules obey van 't Hoff's law, i.e.* the ratios $(\pi_i/C_i) \div RT$ and $(\pi_u/C_u) \div RT$ are not unity.

Behaviour of the Ions.—The osmotic pressure of the ions is *less* than that calculated from the gas law. This is true in every case, except for solutions of lithium chloride 0·1 N and above; hydration is probably the cause of the exceptional behaviour. The behaviour of ions may be represented within the error of the freezing point determinations by an equation of the form—

$$d\pi_i/dC_i = RT(1 + kC_i^m) \quad . \quad . \quad . \quad (14)$$

Behaviour of the Undissociated Molecules.—The osmotic pressure of the undissociated molecules is considerably greater than that calculated from the gas law (van 't Hoff's law). In the case of the chlorides, the deviations continue to increase with the concentration; for the nitrates, a maximum is reached at about 0·02 N. The effect of hydration, according to Bates, is of importance. Hydration is usually considered as increasing the osmotic pressure or the freezing-point lowering of a solution largely by lessening the amount of "free" water in the solution. It has been found, however, by Bates that the osmotic pressures of the several constituents in a given solution are affected to quite a different extent. The influence which hydration has on the ions is less than its influence on the undissociated molecules. Thus in the case of the most highly hydrated salt, lithium chloride, and the slightly hydrated salt, caesium nitrate, at 0·3 N, the difference between the values of the rate of change of osmotic pressure with concentration is 16 per cent. for the ions and 38 per cent. for the undissociated molecules. It is evident that hydration has some effect besides that due to the removal of "free" water.

Electromotive Force of Concentration Cells.—In the preceding chapter (Chap. VII.) it has been shown that the simple osmotic theory of the production of e.m.f. of a cell reversible with respect to the cation leads to the expression—

$$E = \frac{2v}{u + v} \cdot \frac{RT}{nF} \cdot \log p_2/p_1 \quad . \quad . \quad . \quad (16)$$

in which p_2 is the osmotic pressure of the more concentrated solution, p_1 that of the weaker solution. Writing the osmotic pressure of the cation as directly proportional to the concentration, *i.e.* assuming van 't Hoff's for the ion and assuming at the same time that γ as measured by conductivity is correct, we can substitute c_2/c_1 for the ionic concentration in the above expression. On the other hand, by making use of equation (14), which purports to give the true connection between the osmotic

pressure and the concentration of the ion as determined by freezing-point, we obtain for the e.m.f. of the cell the expression—

$$E = \frac{2v}{u+v} \cdot \frac{RT}{nF}\left[\log c_2/c_1 + \frac{k}{m}(c_2^m - c_1^m)\right] \quad . \quad . \quad (17)$$

which reduces to the simpler Nernst expression when $k = 0$. Bates has tested the above expression in connection with certain e.m.f. data obtained by Jahn, which are given in the following table. In addition to the results calculated by (17) there are added for comparison the values obtained by applying the simple expression of Nernst :—

$$E = \frac{2v}{u+v} \cdot \frac{RT}{nF} \cdot \log \frac{c_2}{c_1}.$$

E.M F. of Concentration Cells of Potassium Chloride.

Concentrations.	E.M.F. Observed.	E.M.F. Calculated by	
		Nernst's Equation.	Bates' Equation.
0·04985 : 0·01969	0·02106	0·02183	0·02125
0·03995 : 0·01969	0·01644	0·01644	0·01621
0·03000 : 0·009924	0·02546	0·02620	0·02558
0·01992 : 0·009924	0·01614	0·01654	0·01617

Inspection of the figures shows that equation (17) reproduces the experimental data with considerable accuracy. This agreement, as Bates points out, is not proof independent of that drawn from the freezing-point data that equation (13) expresses the behaviour of ions of potassium chloride. It shows that the freezing-point data and the electro-motive force data are consistent with each other.

The Evaluation of the Degree of Ionisation.—There are, among others, the following three assumptions which may be employed for the calculation of the degree of ionisation :—

1. The degree of ionisation is given by the conductivity-viscosity ratio.
2. van 't Hoff's law is obeyed by the ions.
3. van 't Hoff's law is obeyed by the undissociated molecules.

Experimental data show that in general only one of these assumptions can be true in the case of strong electrolytes. The acceptance of any one compels the rejection of the other two.

Bates points out that the mistake is often made of calculating the degree of dissociation from freezing-point data by using the empirical expression $\pi = iRTc$, which, as already shown, implies that assumptions 2 *and* 3 are simultaneously true. Confining ourselves for the moment to assumptions 2 and 3, it seems desirable to show in another way—somewhat similar to that employed by Washburn (*loc. cit.*) —that the acceptance of the one necessarily leads to the rejection of the other.

The differentiation of the mass law expression $C_i^2/C_u = K$ and the elimination of K from this equation and the derived differential gives—

$$2dC_i/C_i - dC_u/C_u = 0.$$

This relation must hold if the mass law is obeyed. By eliminating C_i and C_u from this equation and from the thermodynamic equation (1), (*viz.* $2d\pi_i/C_i - d\pi_u/C_u = 0$), it is seen that the necessary and sufficient condition that the law of mass action should hold is that at all concentrations $d\pi_i/dC_i = d\pi_u/dC_u$. Now the computation of van 't Hoff's factor "*i*" from freezing-point data, and the consequent calculation of the degree of ionisation on this basis assumes that the ions *and* the undissociated molecules are normal. That is, it assumes

$$d\pi_i/dC_i = d\pi_u/dC_u = RT$$

which is equivalent (compare relation just deduced) to assuming that the law of mass action holds for strong electrolytes, which is contrary to fact. Hence assumptions 2 and 3 cannot hold simultaneously.

It is to be remembered that the quantitative results obtained by Bates for the osmotic pressure of ions and molecules rest on the assumption that the conductivity-viscosity ratio gives a sensibly correct measure of the ionisation.[1] That is, he considers assumptions 2 and 3 as both invalid, and illustrates it by the data already quoted at length in the case of KCl. All the values of π_i and π_u which have been given rest on the truth of the conductivity method. If the conductivity method were shown to be unsound, these values would of course lose their significance. It is therefore very necessary—especially in view of G. N. Lewis's work already alluded to—to examine more closely the conductivity method of determining γ. The arguments in its favour are cited briefly by Bates as follows :—

Kohlrausch's principle of the independent migration of ions affords a theoretical basis for the validity of the conductivity method of determining γ. Kohlrausch's principle gives a picture of the mechanism of electrical conduction in solutions, and the factors upon which conductance depends, *viz.* the number of carriers, the charge upon each, and their mobility. The experimental determination of transport numbers also supports the conductivity method of calculating ionisation. The experimental results show that up to about 0·1 N there is no certain change in the *relative* mobilities of the ions. Bates is here referring to the true transport numbers obtained by means of the reference substance method. These values change much less with the concentration than do the Hittorf numbers.[2]

[1] This does not refer to the criticism of the use of the van 't Hoff factor "*i*" in connection with freezing-point data, which is quite indefensible, as it involves two simultaneous assumptions which are incompatible. The proof, just given, of the invalidity of the "*i*" mode of calculating dissociation is quite independent of the accuracy or inaccuracy of conductivity results.

[2] The constancy of the transport number does not necessarily indicate actual constancy in the absolute mobilities of the ions as the concentration is altered. Suppose that we assume with G. N. Lewis that the mobilities increase as concen-

Of course we must restrict ourselves to dilute solutions in employing the conductivity method, for in concentrated solutions hydration becomes of importance and introduces complications. [Note that we do not say that concentrated solutions must be avoided because the gas law would break down. That reason does not apply at all to conductivity: it does apply to the question of the range over which assumptions 2 and 3 are to be regarded as even approximately true.]

The case of the hydrogen ion is particularly important because of its great mobility. Even in this case Bates considers that the best evidence indicates that its mobility is constant.[1] [If the mobility of an ion, not its transport number, were shown to be independent of concentration the case would be fairly well made out in favour of the conductivity method of determining ionisation].

Bates finally concludes that up to 0·1 N the degree of dissociation may be calculated from the conductivity-viscosity ratio within a few tenths of 1 per cent.

We now turn to assumptions 2 and 3.

Against the method of calculating the degree of ionisation upon one or other of the two assumptions, *viz.* (2) that the ions are osmotically normal or (3) that the molecules are normal, may be urged the objection that the acceptance of one of these two assumptions necessitates the rejection of the other and the conductivity assumption as well. Between the two assumptions (2 and 3) it is difficult to make a choice. They are similar and apparently equally probable. *One* assumption only can be made, and Bates takes the conductivity assumption to be the correct one thereby rejecting both of the assumptions just referred to. This certainly appears to be the logical thing to do.

It is generally held that even though the law of mass action is not obeyed at ordinary concentrations, it must, for thermodynamic reasons hold for the infinitely dilute solution. Even in this case, there is no theoretical reason why $d\pi_i/dC_i$ should be equal to $d\pi_u/dC_u$. The calcu-

tration increases, then if the mobility of each ion increases by the same fractional amount the transport number $u/(u + v)$ will remain constant although $(u + v)$, which determines the conductivity, may have altered. The probability of the increase being the same *fractional* amount for both ions is perhaps not great; and if this probability be negligible then constancy in transport number would actually mean constancy in absolute mobility.

[1] Kendall, *Trans. Chem. Soc.*, 101, 1275 (1912). Kendall's investigation consists of a lengthy series of conductivity measurements carried out with great accuracy. Kendall does not demonstrate explicitly that the mobility of the $H^{\cdot}$ ion is independent of concentration, but what he does show is, that in the case of moderately weak acids there is a single value for the equivalent conductivity at very high dilution $\Lambda\infty$, which, when substituted in the expression $\gamma = \Lambda v/\Lambda_\infty$, gives values for γ which in turn yield very concordant values for the mass action constant—more concordant values than any other assumed value of Λ_∞ would yield. That is, this single value for Λ_∞ is truly comparable with the various values Λv obtained at other concentrations in the sense that the resulting γ values fit the mass action expression. The fact that a *single* value for Λ_∞ is sufficient indicates that all the Λv's are comparable with one another, *i.e.* that the mobility is really remaining constant at the various dilutions. The acids chosen by Kendall are moderately weak, the choice being determined by considerations which Kendall's paper makes clear.

lations which have preceded show that these ratios at ordinary concentrations may be expressed by equations, which extrapolated to infinite dilution, do give the same value, RT, for both. This *empirical* fact probably affords the best basis for the belief that at infinite dilution the law of mass action is obeyed by solutions of strong electrolytes.

There is nothing in the simple form of the electrolytic dissociation theory which necessitates the conclusion that the ions and the undissociated molecules of an electrolyte should obey van 't Hoff's law. If they do not obey this law the law of mass action cannot be obeyed. Hence the fact that solutions of strong electrolytes deviate from the requirements of the law of mass action is no argument against the theory of electrolytic dissociation.[1]

As we have seen, the present position with regard to the so-called anomaly of strong electrolytes may be put thus: There are *three* possible assumptions to be considered, the acceptance of any *one* of which involves the rejection of the other two. In the light of this conclusion we must revert to the question already proposed on p. 225 of Vol. I., *viz.* "Is the law of mass action in error or does the ratio of the equivalent conductivities not give the true measure of the ionisation?"

It will now be evident that the form in which this question is put is open to serious criticism. By putting the question in the form of a simple alternative it is implied that if one hypothesis is right the other is wrong. It is to be remembered, however, that there are three hypotheses, not two, involved in the problem. The law of mass action requires two assumptions to be simultaneously satisfied, *viz.* normality in behaviour of ions *and* molecules, and hence the law of mass action in the case of strong electrolytes is incompatible with the conclusions of Bates, whether the conductivity results are right or wrong. In other words the conductivity method may be correct (Bates' view) and simultaneously the law of mass action breaks down because neither of the species obeys the gas law. The law of mass action is therefore breaking down in a double sense because the abnormality of even one species would be sufficient to invalidate it.

The experimental facts would be satisfied by any *one* of the following three sets of conditions:—

1. (*a*) Conductivity results correct. (*b*) Molecules abnormal. (*c*) Ions abnormal in the osmotic sense.

2. (*a*) Conductivity results incorrect. (*b*) Molecules normal. (*c*) Ions abnormal.

3. (*a*) Conductivity results incorrect. (*b*) Molecules abnormal. (*c*) Ions normal.

It will be observed that in no case do we find the condition that the molecules *and* the ions are simultaneously normal, as this would involve the applicability of the law of mass action, which, in strong electrolytes, is contrary to fact.

On the whole hypothesis (1) appears to be the correct one.

[1] It will be observed that in the treatment here followed we are not considering the more recent investigations of Ghosh, Bjerrum and others who have come to the conclusion that in solutions of strong electrolyte dissociation is complete and therefore the Arrhenius expression is incorrect.

On referring back to the table for KCl given by Bates, it will be observed that whilst the ions *and* the molecules are abnormal in osmotic behaviour, the abnormality of the undissociated molecules is much the greater of the two. In fact the behaviour of the ions is not very far removed from the normal as is shown by the figures of column IX., in which the ratio (which should be unity) varies from 0·962 to 0·989.

As a first approximation therefore we may regard the ions as very nearly normal. In the light of this approximately true statement we are in a position to appreciate the considerations put forward by J. Walker in his presidential address to section B., British Association, 1911.

Reaction Velocity in Relation to the Osmotic Behaviour of Ions and Molecules.

Walker assumes that the conductivity method is valid. Discussing the anomaly of strong electrolytes from the point of view of the van 't Hoff dilution law—an empirical and only approximately true expression—Walker points out that this expression may be written in several ways, one of which throws the abnormality upon the undissociated molecule, *viz.* $C_i^2/C_u^{1\cdot33}$ = constant. [It must be borne in mind that we are only dealing with approximations. Having assumed that conductivity method is correct we now know that the ions as well as the molecules must be abnormal; the abnormality of the ions is not marked however.]

Let us suppose that we have found a reaction in which either the ionised or unionised portion of an abnormal electrolyte is converted into a third substance with measurable velocity. Such a reaction actually exists in the transformation of ammonium cyanate into urea, in aqueous and aqueous-alcoholic solutions. There is evidence that it is the ions which directly yield the urea, but for the moment this is left open. Suppose, first, that the unionised cyanate is transformed directly into urea. Then we have the successive reactions—

$$NH_4^{\cdot} + CNO' \rightleftarrows NH_4CNO \rightarrow CO(NH_2)_2.$$

If the unionised substance behaves normally, then the conversion of the ammonium cyanate into urea, when referred to the unionised substance will appear unimolecular, and obey the law of mass action; when referred to the ions it will not appear to be bimolecular and will not obey the law of mass action. Suppose now that the direct formation of urea is from the ions. We are then dealing with the reactions—

$$NH_4CNO \rightleftarrows NH_4^{\cdot} + CNO' \rightarrow CO(NH_2)_2.$$

Again let us assume the unionised substance to be normal. Once more, if the transformation is referred to the unionised substance it will appear as monomolecular; when referred to the ions it will not appear as bimolecular, as it should if the law of mass action were obeyed by the ions. It is a matter of indifference then, so far as the point with which we are dealing is concerned, whether the ionised or unionised cyanate is transformed directly into urea. If the unionised cyanate behaves normally the action when referred to it (the unionised cyanate)

will in either case appear to be strictly monomolecular. If the ions on the other hand behave normally, the reaction when referred to them will be bimolecular and normal; when referred to the unionised cyanate it will not be monomolecular and therefore would be abnormal. The actual experiments show that whether water or a mixture of alcohol and water be taken as solvent, the reaction when referred to the ions is strictly bimolecular; when referred to the unionised substance it is not monomolecular, *i.e.* it is not directly proportional to C_u, but is rather proportional to a power, namely, $C_u^{1.4}$.

It will be observed that even very accurate velocity constants are not able to detect the slight abnormality of the ions—which must exist if the conductivity method is valid—whilst the abnormality of the undissociated molecules on the other hand is quite apparent, and further the power to which C_u must be raised is very similar to the value obtained by van t' Hoff for a strong electrolyte. These results of Walker bear out in a striking manner the conclusion arrived at on quite other grounds by Bates, regarding the magnitude of the abnormal behaviour of the undissociated molecules.

It must be pointed out further that the principle of the constancy of the value of the "ionic product" affords additional evidence that the ions act in a more nearly normal manner than do the undissociated molecules. This is evident from the work of Noyes and his collaborators already referred to in Vol. I., Chap. VII.

Ionisation in Formic Acid Solutions.

The validity of the conductivity method of determining the degree of ionisation of *salts* receives further support from measurements in anhydrous formic acid as solvent. Thus Schlesinger and Coleman (*Jour. Amer. Chem. Soc.*, **38**, 271, 1916) have determined by this method the ionisation of the alkali formates. Formic acid resembles water in being an excellent dissociating medium. The dissolved formates are highly ionised, *i.e.* a decinormal solution of sodium formate is ionised to the extent of 88 per cent. at 18° C., and similar values are obtained for the lithium, rubidium, and caesium salts. In spite of this extensive ionisation, however, these electrolytes obey the law of mass action with a high degree of accuracy.

Recently Schlesinger and Mullinix (*Journ. Amer. Chem. Soc.*, **41**, 72 (1919)) have extended the investigation to the formates of the divalent metals, calcium and strontium. Again, the degree of ionisation is large. The concentration range examined extended from 0·04 to 0·4 gram-equivalents per liter. It is now found that whilst the law of mass action is obeyed over a considerable range—from 0·1 to 0·3 gram-equivalents per liter—the law does not apply to regions above and below these limits. The mechanism of ionisation in this solvent and the law which it obeys represent an unsolved problem. In general, in the case of non-aqueous solvents the data are so meagre and in some cases so conflicting that no definite statements can be made about them at the present time.

The Ionisation and Activity of Strong Electrolytes in Aqueous Solution.

Considerations Based on E.M.F. Data

(*cf.* Noyes and MacInnes, *Journ. Amer. Chem. Soc.*, **42**, 239 (1920)).

The degree of ionisation of an electrolyte which we shall denote throughout by γ is usually regarded as obtainable from measurements of equivalent conductivity, *i.e.* $\gamma = \Lambda_v/\Lambda_\infty$ or, if we allow approximately for the change in viscosity of the solution, $\gamma = \Lambda_v\eta_v/\Lambda_\infty\eta_\infty$. This point of view is adopted in dealing with ionisation in Vol. I. For the present we shall continue to adopt it when speaking of actual ionisation. It means that we are regarding the conductivity method as giving a correct measure of the *number* of ions present in a dilute solution. Towards the end of this chapter it will be necessary to refer to some recent work dealing with the question as to whether ionisation really does increase with dilution in the case of strong electrolytes. For the present, however, we begin with the assumption discussed already in connection with Bates' investigation that the degree of ionisation is a function of dilution and is given by the conductivity method.

It was first clearly pointed out by G. N. Lewis that the e.m.f. of concentration cells containing dilute solutions of strong electrolytes could not be *accurately* expressed by the logarithmic formula of Nernst (discussed in the preceding chapter) if the values attached to the concentrations of the ions in the two solutions were those obtained by the conductivity method, *i.e.* from the ordinary degree of ionisation. In order to make the simple logarithmic formula fit the observed e.m.f of a concentration cell, it is necessary to choose other numerical values in the logarithm to which Lewis gives the name the *activities* or *effective concentrations* of the ions. Thus, instead of writing the e.m.f., E, of a concentration cell (with transport) in which the liquid/liquid P.D. has been annulled in the form—

$$E = \frac{RT}{nF} \log_e \frac{\gamma_1 c_1}{\gamma_2 c_2}$$

where c_1 and c_2 are the total concentrations of the two solutions of strong electrolyte respectively, and γ_1 and γ_2 are the degrees of ionisation of the electrolyte as measured in the ordinary way (whence $\gamma_1 c_1$ and $\gamma_2 c_2$ stand for the actual concentration of one of the ions), say, the cation, in the two solutions, Lewis writes—

$$E = \frac{RT}{nF} \log_e a_1 c_1/a_2 c_2$$

where c_1 and c_2 have the same significance as before, and α_1 and α_2 are the so-called *activity coefficients* or *thermodynamic degrees of ionisation* of either of the ions in the two solutions. The products $\alpha_1 c_1$ and $\alpha_2 c_2$ are the respective activities of either of the ions or their effective concen-

trations. These products (activities) are frequently denoted by the symbols a_1 and a_2, that is—

$$E = \frac{RT}{nF} \log_e a_1/a_2.$$

The fundamental fact is that in general the α values are not identical with the γ values.

An e.m.f. measurement only gives the ratio of the activities of an ion at two total salt concentrations. In order to obtain individual values for $\alpha_1 c_1$ and $\alpha_2 c_2$, and therefore for α itself, at any dilution ($1/c$), Lewis makes the reasonable assumption that at very great dilution, beyond 1/1000 N, the value of α is sensibly identical with the value of γ: both of them approximating to unity in the limit. It is clear that we are regarding both α and γ as functions of the dilution.

From a series of e.m.f. measurements using concentration cells down to considerable dilutions it is thus possible to calculate the values of α for the ions of the electrolyte. It will be observed that at any given dilution we ascribe the same value of α to the cation as to the anion. In the case of γ this is of course inevitable. It is of interest to compare the values of γ for a few simple salts at various dilutions with the corresponding values of α. The necessary data have been obtained by MacInnes and Parker (*Journ. Amer. Chem. Soc.*, **37**, 1445 (1915)) in the case of KCl; by Ellis (*ib.* **38**, 737 (1916)) and Noyes (*ib.* **39**, 2532 (1917)) in the case of HCl; by MacInnes, Beattie and Chow (*cf.* Noyes and MacInnes, *ib.* **42**, 239 (1920)), and Chow (*ib.* **42**, 488 (1920)), also MacInnes and Beattie (*ib.* **42**, 1117 (1920)) in the case of LiCl and of KOH. The type of cell employed by MacInnes and his collaborators for the purpose of calculating α values is one without transport, *e.g.*—

Ag	AgCl, KCl(c_2)	K_xHg	KCl(c_1), AgCl	Ag

It has already been shown in Chap. VIII. that the e.m.f. of such a cell is given by—

$$E = \frac{RT}{F} \log_e K_1^+ Cl_1^- / K_2^+ Cl_2^-.$$

Assuming the activities of the cation and of the anion in any solution to be the same, this becomes—

$$E = \frac{RT}{F} \log_e (a_1 c_1)^2/(a_2 c_2)^2 = \frac{2RT}{F} \log_e a_1 c_1/a_2 c_2.$$

The following table contains the values of the activity coefficients α thus obtained from e.m.f. measurements, as well as the values of γ as determined by conductivity measurements, allowance being made for the change in viscosity of the solution on dilution, *i.e.* $\gamma = \Lambda_v \eta_v / \Lambda_\infty \eta_\infty$.

COMPARISON OF ACTIVITY COEFFICIENTS (α) WITH DEGREES OF IONISATION (γ).

c. Moles of Electrolyte per 1000 grams water.	α.				γ.			
	KCl.	LiCl.	HCl.	KOH.	KCl.	LiCl.	HCl.	KOH.
0·001	0·979	0·976	—	—	0·979	0·976	0·990	—
0·003	0·943	0·945	0·990	0·982	0·968	0·962	0·986	0·980
0·005	0·923	0·930	0·965	0·975	0·956	0·949	0·981	0·975
0·010	0·890	0·905	0·932	0·961	0·941	0·932	0·972	0·963
0·030	0·823	0·848	0·880	0·920	0·914	0·899	0·957	0·939
0·050	0·790	0·817	0·855	0·891	0·889	—	0·944	0·925
0·100	0·745	0·779	0·823	0·846	0·860	0·834	0·925	0·910
0·200	0·700	0·750	0·796	0·793	0·827	—	0·909	0·891
0·300	0·673	0·738	0·783	0·769	0·807	0·759	0·903	0·889
0·500	0·638	0·731	0·773	0·765	0·779	—	0·890	0·884
0·700	0·618	0·734	0·789	0·772	0·761	—	0·874	0·879
1·000	0·593	0·752	0·829	0·786	0·742	0·641	0·845	0·877
2·000	(0·572)	—	1·040	—	—	—	—	—
3·000	(0·586)	1·164	1·402	—	—	0·458	—	—

[The values of α in the KCl column enclosed in brackets are obtained from Harned's data (*Journ. Amer. Chem. Soc.*, **38**, 1989 (1916)). The values of α in the case of KCl should be compared with the values calculated from the freezing point data by Lewis and Linhart, quoted later; the values obtained from the freezing point are somewhat higher than those obtained from e.m.f. data. Theoretically, they should be identical, except in so far as temperature may exert a small effect. The e.m.f. data refer to 25° C., the freezing point data to 0° C. approximately.]

The results given in the above table may be summarised as follows:—

1. In the case of all four substances the activity coefficient α decreases with increasing concentration much more rapidly than does the value of γ, the difference amounting to from 7 per cent. to 15 per cent. at 0·1 molar, and from 5 per cent. to 18 per cent. at 0·5 molar.

2. In the case of all the substances except KCl, α passes through a minimum in the neighbourhood of 0·5 molar, afterwards rapidly increasing at the higher concentrations. Even KCl, according to Harned's data, has a minimum activity coefficient in the neighbourhood of 2 molar.

3. The activity coefficient, even at moderate concentrations, varies considerably with the nature of the substance; thus at 0·5 molar the value of 100 α is 63 per cent. for KCl, 73 per cent. for LiCl, and 77 per cent. for HCl and KOH.

The general conclusions to be drawn from these observations are (1) that conductivity measurements leading to the quantity γ do not give even approximately a measure of the activity of the ions, except at very great dilution, and (2) that the activity varies with the concentration differently in the case of different substances.

The most striking fact which emerges in connection with α is that it passes through a minimum, whilst the value of γ varies with the dilution in a perfectly regular manner. This of itself indicates that the activity coefficient is something fundamentally different from the so-called degree of ionisation.

Up to this point we have been regarding the activity and activity coefficients of ions as essentially quantities which can be determined from e.m.f. measurements, the values of $a = \alpha c$ (the activity) being those which will account for the observed e.m.f. of concentration cells when substituted in the *logarithmic formula*. The logarithmic formula in this case arises from an integration in which the gas law has been assumed (*cf.* Chap. VII.). By making use of the formula at all we are really assuming that the osmotic pressure π of each of the ionic species is related not to the concentration of the ion but to the activity by the expression: $\pi_{ion} = RT\alpha c = RTa$.

In this way we are defining activity as a quantity characteristic of a certain species which is related to the osmotic pressure of the species quantitatively by the gas law. The same relationship is supposed to hold good for the activity of the undissociated molecule. It will have been clear from the thermodynamic treatment followed in the preceding chapters of this volume that several other important physico-chemical generalisations and expressions are equally dependent in their usual form upon the applicability of the gas law. In fact, such expressions as the law of mass action, the lowering of freezing point, lowering of vapour pressure of solutions, rise of boiling point, and the logarithmic expression for the e.m.f. of concentration cells are all mutually interdependent, in the sense that they involve not only the two laws of thermodynamics, about which there can be no doubt, but also the assumption that the gas law is valid for dilute solutions. All these different expressions, for the investigation and measurement of which different experimental procedure is necessary, should logically involve the activity coefficient term, α, not the γ term, and, further, the values obtained for α by these various modes of investigation should be sensibly identical. The concept of activity is therefore one of wide significance. In fact, the activity of a molecular or ionic species may be identified with its general chemical reactivity, and should, therefore, be the significant quantity in chemical kinetics as well as in chemical statics.

It is necessary to point out, however, that whilst this method of treatment is justifiable, it does not afford any "molecular" picture of what activity is, for the simple reason that our definition is essentially a thermodynamic one. A tentative attempt to visualise activity a little more clearly is given later. For the present, however, it is necessary to indicate more closely the thermodynamic inter-relationships referred to above.

We commence therefore with the fundamental definition that the *activity of a substance* (*not necessarily an ion*) *is its effective concentration from the point of view of mass action;* that is, on substituting the activi-

ties of the various reactants and resultants in the mass action expression a true equilibrium constant, independent of the dilution, is necessarily obtained.

In connection with the expression for the law of mass action there is a point which may be emphasised. Suppose that numerical values for the activity of the ions of a binary electrolyte have been obtained, say, from e.m.f. measurements. In order to evaluate the expression for the equilibrium constant "K" it is correct to substitute the values of a^+ and a^- (the activities of the positive and negative ions), in the numerator of the expression, but it is not correct to write $(1 - a)$ as the denominator; for, having discarded the simpler idea of concentration or mere number of ions, we are not justified in supposing that the activity of the undissociated molecules is obtained numerically by simply subtracting the a term of either ion from unity. If we were to do so we would obtain values for "K" which would not be constant, but would show a rapid rise as the concentration of the electrolyte increases. Instead, we must measure the true activity of the undissociated molecules by some independent method, say, by measuring the partial pressure of the undissociated molecules in the vapour phase above the solution, and substitute the value so obtained in the denominator of the mass action expression. On doing this the value of "K" must remain constant from the very definition of activity. Whilst the activity of the ions can be usually measured fairly conveniently by the e.m.f. method, it is more difficult to obtain values for the activity of the undissociated molecules, owing to the fact that the vapour pressure method cannot be employed with the numerous *non-volatile* strong electrolytes. As an alternative mode of treatment in this case we might possibly make use of a result obtained by Washburn and Wieland (*Journ. Amer. Chem. Soc.*, **40**, 106-158 (1918)) at extreme dilution. The result depends upon the applicability of the conductivity method, but we are referring to a dilution so great that we may identify the concentrations with the activities. These authors have found that the mass action expression as ordinarily expressed in concentration terms appears to reach a really constant value, namely, 0·02 (using the grammolecule per liter as unit of concentration), the same for all strong binary electrolytes. Taking this value as the correct one for *all* dilutions, and knowing the activity of the ions at any concentration we could calculate the activity of the undissociated molecule as a function of dilution. Incidentally it would be necessary to ascribe to the activity of the undissociated molecules a value which is *greater* than their ordinary concentration in order to obtain a constant value for "K". On the other hand, it has been pointed out that the activity of an ion over a wide range of concentration is *less* numerically than its concentration as determined from conductivity results. Only at high concentration of the electrolyte does the activity of the ions become greater than their apparent concentration. Hence the ions appear to behave, in respect of activity, at *high* concentration in a manner analogous to that of the undissociated molecule at all concentrations.

We have been considering the law of mass action as expressed in terms of the activities of the ions and molecules. We have also considered the determination of the activities of ions by means of e.m.f. measurements. It is now necessary to consider the activity of the ions from the point of view of the solubility product.

Solubility Product and Ionic Activities

(*cf.* G. N. Lewis (*Journ. Amer. Chem. Soc.*, **34**, 1633 (1912)).

"If a solid salt, such as thallous chloride, is in equilibrium with its ions, then if a_1 is the activity of one ion and a_2 is that of the other, it is thermodynamically necessary that the product $a_1\ a_2$ should always remain constant at a given temperature. Now it is shown in the paper of Bray (*Journ. Amer. Chem. Soc.*, **33**, 1683 (1911)) that the product of the concentrations C_1 and C_2 of the ions does not remain constant, but increases with increasing total ion concentration in every case studied. This was shown to be true for thallous chloride and for potassium perchlorate in presence of other uni-univalent salts. This shows that for at least one of the ions the ratio a/C falls off with increasing ion concentration. The product $a_1\ a_2$ is constant, and therefore between any two solutions it is evident that $C_1C_2/C'_1C'_2$ is equal to—

$$(a'_1/C'_1 \times a'_2/C'_2) \div (a_1/C_1 \times a_2/C_2).$$

Now introducing the assumption that both ions behave alike, we have—

$$C_1C_2/C'_1C'_2 = (a'_1/C'_1)^2 \div (a_1/C_1)_2 = (a'_2/C'_2)^2 \div (a_2/C_2)^2.$$

Thus from the change in the solubility product we can find the way in which the ratio a/C varies for each ion. The following table contains a summary of some of the results thus obtained, and includes a number of data obtained from an earlier paper of Noyes (*Zeitsch. physik. Chem.*, **9**, 603 (1892)). In each case $C'_1C'_2$ is taken as the extrapolated value for infinite dilution of the solubility product.

"This extrapolation is performed by plotting the solubility product against the total ion concentration as this seems to be the predominant factor which causes the variation. This extrapolation in the case of thallous chloride is entirely reliable. In the case of the much more soluble salt, patassium perchlorate, it is very rough, and is only made to render the results for this salt comparable with those for thallous chloride.

Solid Salt.	Added Salt.	Percentage Diminution in a/C at			
		0·02 Molar.	0·05 Molar.	0·1 Molar.	0·2 Molar.
TlCl	KCl	4	8	13	18
TlCl	NaCl	4	8	13	19
TlCl	NH_4Cl	4	8	—	20
TlCl	HCl	4	7	9	12
TlCl	$TlNO_3$	4	8	13	—
TlCl	KNO_3	4	7	10	—
$KClO_4$	KCl	—	—	9	12

"The last four columns show the percentage diminution in the ratio a/C for the ions, between zero (added) salt concentration and the concentration given at the head of each column. The results are very striking and show the generality of the lowering of the ratio of a/C with increasing salt or ion concentration. In the case of HCl the degree of dissociation is assumed to be the same as that of KCl at each concentration."

Passing now from the activity of ions we turn to a consideration of the activity of undissociated molecules as deduced from vapour pressure measurements.

Determination of the Activity of Molecules by means of Vapour Pressure Measurements.

It has already been pointed out that we may take the vapour pressure of a substance as a measure of its active mass, and therefore of its activity. In the case of homogeneous reactions in *gases* it may be recalled that the law of mass action has been fully verified, the terms employed in the expression for "K" being simply the concentration terms of the various constituents. In the case of gases, and therefore in the case of vapours at low concentrations, the concept of activity becomes identical with concentration. On this basis the relative activities of the undissociated molecules of an electrolyte will be correctly measured at various concentrations of the solution by determining the values of the partial pressure of the molecules in the vapour in equilibrium with the solutions. In the majority of cases the undissociated molecules of strong electrolytes are not sufficiently volatile to become measureable in this way. There are, however, a few electrolytes in which this is possible, namely, aqueous solutions of HCl, HBr, and HI.

Consider two solutions of HCl of different *total* concentrations c_1 and c_2. Suppose that p_1 is the pressure due to the HCl molecules over the one solution, and p_2 the pressure of the molecules over the other solution. Then, if the activities of the *un*dissociated molecules in the solutions be a_1 and a_2, it follows that—

$$p_1/p_2 = a_1/a_2.$$

The values of the vapour pressures of the halide acids over their aqueous solutions have been determined by Bates and Kirschman (*Journ. Amer. Chem. Soc.*, **41**, 1991 (1919)). Briefly, the method employed is to determine the amount of HCl or of HBr or of HI contained in a given quantity of air (or of nitrogen in the case of HI) in equilibrium with the aqueous solution, and to compare this with the amount of water vapour which the same air contained when in equilibrium with pure water at the same temperature. From a knowledge of the vapour pressure of water at the temperature of the experiment, the vapour pressure of the halide may be computed. In the case of HCl the error in the values of the halide pressure at 25° C. is 2·8 per cent., in the case of HBr, 7 per cent., and in the case of HI, 10 per cent. The following table contains a summary of the results obtained at 25°C.:—

Vapour Pressures of the Hydrogen Halides over their Aqueous Solutions at 25° C.

Moles of Halide per 1000 grams H_2O.	Vapour Pressure in mms. Mercury.		
	HCl.	HBr.	HI.
4·0	0·0182	—	—
5·0	0·0530	—	—
6·0	0·140	0·00151	0·00057
7·0	0·348	0·00370	0·00182
8·0	0·844	0·0089	0·0065
9·0	1·93	0·0226	0·0295
10·0	4·20	0·059	0·132
11·0	—	0·151	—

It will be observed that the values are very small, and can only be measured with reasonable accuracy in the case of concentrated solutions. This is a considerable drawback to the method from the point of view of the activity of molecules in dilute solution. Naturally, these pressure values are not identical with, but are strictly proportional to, the activity of the undissociated molecule in solution.

To show the connection between the partial pressures of the undissociated molecules of, say, HCl and the e.m.f. of a concentration cell involving HCl, we shall first of all revert to the law of mass action as expressed in terms of activities.

Suppose that a_1^+ and a_1^- denote the activities of the positive and negative ions in the HCl solution of total concentration c_1, the symbols a_2^+ and a_2^- denoting similar quantities in the solution c_2. Then, if a_1 and a_2 are the activities of the undissociated molecules respectively in the two solutions, the law of mass action requires that—

$$\frac{a_1^+ \times a_1^-}{a_1} = \frac{a_2^+ \times a_2^-}{a_2}$$

or $$a_1/a_2 = (a_1^+ \times a_1^-)/(a_2^+ \times a_2^-) = c_1^2 a_1^+ a_1^- / c_2^2 a_2^+ a_2^-$$

where a is in general the activity coefficient for any ion.

If we imagine one mole of HCl transferred *via* the vapour from solution c_1 to the solution c_2, the maximum work done, A, or free energy decrease, is given by—

$$A = RT \log p_1/p_2.$$

Since $p_1/p_2 = a_1/a_2$, it follows that we can write:—

$$A = RT \log c_1^2 a_1^+ a_1^- / c_2^2 a_2^+ a_2^- = RT \log (a_1^+ a_1^-)/(a_2^+ a_2^-).$$

Further, if we assume that the activity of the cation in a given solution is the same as that of the anion, we can transform the above relation into—

$$A = 2RT \log a_1^+/a_2^+ = 2RT \log a_1 c_1/a_2 c_2.$$

Instead of transferring the mole of HCl *via* the vapour we may transfer it by the passage of one faraday of electricity through a concentration cell (without transport) of the type—

$$H_2 \mid HCl(c_2), AgCl \mid Ag \mid AgCl, HCl(c_1) \mid H_2$$

the e.m.f. of which is E. Since A = EF it follows that—

$$E = \frac{RT}{F} \log p_1/p_2 = \frac{2RT}{F} \log a_1c_1/a_2c_2.$$

$$= \frac{RT}{F} \log_e (a_1^+c_1)(a_1^-c_1)/(a_2^+c_2)(a_2^-c_2).$$

which is the expression already obtained in Chap. VII. for the e.m.f. of such a cell. It is convenient to employ this type of cell in the present case because the passage of one faraday corresponds precisely to the effective transfer of one mole of HCl. In the case of a cell with transport it would be necessary to employ more than one faraday. A definite relation exists, however, between the e.m.f. in the latter case and the work term A, as has already been shown in connection with Helmholtz's method of determining the transport number of an ion (Chap. VII.).

Bates and Kirschman tested the accuracy of their vapour pressure data by equating the two expressions, EF and RT $\log p_1/p_2$, where E is the e.m.f. of a cell without transport. This equality may be written in the following way :—

$$\log_{10} p_1 = \log_{10} p_2 + EF/2{\cdot}303RT$$

p_2 was taken as the vapour pressure corresponding to a decinormal solution, this being chosen as an arbitrary standard. On this basis it follows that the graph obtained by plotting values of $\log_{10} p$ against the corresponding values of $E_{obs.}$ should be a straight line, having the slope $F/2{\cdot}303RT$. The relationship was verified satisfactorily in this manner.

Calculation of the Activity of Ions as a Function of Dilution, from Freezing Point Data.

As already pointed out the apparent molecular weights of dissolved substances—and consequently the thermodynamic degree of ionisation or activity coefficient α in the case of an electrolyte—as determined by freezing point data are necessarily those which would be obtained from direct measurements of osmotic pressure or from e.m.f. measurements, since these different modes of measurement are related thermodynamically. It will be recalled that the activity coefficient α for an ion is less than the γ value over a wide range of concentration.

The freezing point method has not been much employed in this connection because of the possible large experimental error. There are, however, a certain number of observations of lowering of freezing point which are sufficiently accurate for a reliable determination of α. These have been correlated by G. N. Lewis and Linhart (*Journ. Amer. Chem. Soc.*, **41**, 1951 (1919)). These authors make use of a simple empirical expression connecting the lowering of the freezing point with the concentration of the salt. The advantage of this method lies in the fact that the theoretically sound expression, deduced by G. N. Lewis, connecting the free energy of dilution, and therefore the activity of the

ions, with the lowering of the freezing point, is complicated and does not lend itself to extrapolation to high dilutions. The empirical equation of Lewis and Linhart is not only convenient but also very accurate. It may be written in the form—

$$nk - t/c = \beta . c^m \quad . \quad . \quad . \quad . \quad (1)$$

where n is the number of ions into which a molecule of the salt ionises; k is the theoretical "molecular depression of freezing point" (in the case of water, $k = 1{\cdot}858°$ per mole of solute in 1000 grams of solvent); t is the observed lowering of freezing point, produced by a salt at concentration c (number of moles of solute per 1000 grams of water); β and m are constants. The applicability of the formula is shown in a number of cases cited in the original paper.

In order to obtain the thermodynamic degree of ionisation, α, Lewis and Linhart combine the above empirical expression with the thermodynamic equation connecting the free energy of dilution with the lowering of freezing point, finally arriving at the following useful formula:—

$$\log_{10}\alpha = -\beta(m + 1)c^m/2{\cdot}303nk^m \quad . \quad . \quad (2)$$

The table on p. 227 contains the values computed by Lewis and Linhart by means of equation (2) for a series of electrolytes over a considerable range of dilution. Equation (1), and consequently equation (2), cannot be applied to solutions of greater concentration than 0·1N.

In order to appreciate the difference between the values of α given in the table (p. 227) and the values of γ obtained from the conductivity expression the reader is referred to the measurements of Noyes and Falk, part of whose data have already been given in Vol. I.

The divergence between α and γ is very pronounced, even in very dilute solutions. The greatest divergence occurs in the case of $CuSO_4$ (*cf.* G. N. Lewis and Lacy, *Journ. Amer. Chem. Soc.*, **36**, 804 (1914)). In order to show how great this difference is, a table, given by Lewis and Linhart, is inserted here. The molar concentration of each salt is 0·01.

Salt.	KCl.	NaCl.	KIO_3.	$NaIO_3$.	K_2SO_4.	$BaCl_2$.	$CdSO_4$.	$CuSO_4$.	$Li(NO_3)_2$.
α =	0·925	0·925	0·872	0·872	0·687	0·716	0·338	0·290	0·571
γ =	0·941	0·936	0·928	0·917	0·872	0·883	0·614	0·629	0·805

Even at M/1000 the α value for $CuSO_4$ is 0·526, whilst the γ value is 0·862.

The Activities and Activity Coefficients of Individual Ions in Strong Electrolytes.

In the foregoing discussion of the various methods whereby values may be obtained for the activities (a) of the ions, it has been assumed that the activity has the same value for the positive as for the negative

PERCENTAGE THERMODYNAMIC DEGREES OF IONISATION (100α) FROM FREEZING POINT DATA.

Molar Concentrations.	$(10)^{-1}$.	$5(10)^{-2}$.	$2(10)^{-2}$.	$(10)^{-2}$.	$5(10)^{-3}$.	$2(10)^{-3}$.	$(10)^{-3}$.	$5(10)^{-4}$.	$2(10)^{-4}$.	$(10)^{-4}$.	$5(10)^{-5}$.	$2(10)^{-5}$.	$(10)^{-5}$.	$5(10)^{-6}$.	$2(10)^{-6}$.	$(10)^{-6}$.	$5(10)^{-7}$.	$2(10)^{-7}$.	$(10)^{-7}$.	$5(10)^{-8}$.	$2(10)^{-8}$.	$(10)^{-8}$.
KCl . .	—	—	89·0	92·5	94·6	96·7	97·7	98·4	99·0	99·3	99·5	—	—	—	—	—	—	—	—	—	—	—
NaCl . .	—	—	89·0	92·5	94·6	96·7	97·7	98·4	99·0	99·3	99·5	—	—	—	—	—	—	—	—	—	—	—
KIO_3 . .	68·4	75·6	83·0	87·2	90·4	93·5	95·2	96·4	97·6	98·2	98·7	99·1	99·4	99·5	—	—	—	—	—	—	—	—
$NaIO_3$ . .	68·4	75·6	83·0	87·2	90·4	93·5	95·2	96·4	97·6	98·2	98·7	99·1	99·4	99·5	—	—	—	—	—	—	—	—
K_2SO_4 . .	—	—	61·5	68·7	74·9	81·4	85·3	88·5	91·7	93·5	95·0	96·4	97·2	97·8	98·3	98·8	99·1	99·4	99·5	—	—	—
H_2SO_4 . .	—	—	—	61·7	69·6	78·2	83·1	87·1	91·0	93·2	94·8	96·5	97·3	98·0	98·6	98·9	99·2	99·5	—	—	—	—
$BaCl_2$ . .	—	—	—	71·6	77·1	83·0	86·5	89·4	92·3	93·9	95·3	96·6	97·3	97·9	98·5	98·8	99·1	99·4	99·5	—	—	—
$CoCl_2$ . .	—	—	—	73·1	78·4	84·0	87·3	90·0	92·7	94·3	95·5	96·8	97·5	98·0	98·6	98·9	99·2	99·4	99·5	—	—	—
$CdSO_4$ . .	—	—	—	33·8	42·0	52·6	59·8	66·3	73·8	78·4	82·4	86·6	89·1	91·2	93·4	94·7	95·8	96·8	97·5	98·0	98·5	98·8
$ZnSO_4$ . .	—	—	—	33·8	42·0	52·6	59·8	66·3	73·8	78·4	82·4	86·6	89·1	91·2	93·4	94·7	95·8	96·8	97·5	98·0	98·5	98·8
$MgSO_4$. .	—	—	—	35·0	42·5	52·0	58·6	64·7	71·7	76·2	80·1	84·4	87·1	89·3	91·7	93·2	94·4	95·7	96·5	97·1	97·8	98·2
$CuSO_4$ . .	—	—	—	29·0	36·2	45·7	52·6	59·0	66·6	71·6	76·0	80·9	84·0	86·7	89·6	91·4	92·8	94·4	95·4	96·2	97·1	97·6
$K_3Fe(CN)_6$	—	—	—	57·1	65·7	75·2	80·8	85·3	89·7	92·2	94·1	96·0	97·0	97·7	98·5	98·8	99·1	99·4	99·5	—	—	—
$La(NO_3)_3$.	—	—	—	57·1	65·7	75·2	80·8	85·3	89·7	92·2	94·1	96·0	97·0	97·7	98·5	98·8	99·1	99·4	99·5	—	—	—

ions in any given solution. If the cation and anion in any given case do not possess identical activity then the numerical values obtained on the basis of the foregoing considerations, e.m.f., vapour pressure, lowering of freezing point, etc., are "average" values, the "average" being equal to $\sqrt{a^+ a^-}$, where a^+ is the activity of the cation and a^- is the activity of the anion.

The first attempt to get at the activity of individual ions has been made by MacInnes (*Journ. Amer. Chem. Soc.*, **41**, 1086 (1919)), the ion considered being the hydrogen ion. As will be seen, it is necessary to assume that in a solution of KCl the cation and anion possess identical activity at any given dilution. For this special treatment of KCl, MacInnes gives certain reasons which appear to make the conclusion fairly reasonable. In his method of attacking the problem MacInnes begins by considering, not the activity of an ion, but the values of γ as determined by conductivity for a number of chlorides. The account of this investigation is expressed largely in MacInnes's own words.

As already mentioned, G. N. Lewis came to the conclusion (though he afterwards modified the conclusion, *cf. Journ. Amer. Chem. Soc.*, **39**, 2258 (1917)) that hydrochloric acid and the alkali chlorides have the same degree of ionisation at the same concentration. This was based upon the relation—

$$\gamma_1/\gamma_2 = \Lambda_1 n_1/\Lambda_2 n_2$$

derived by Tolman on the assumption that the chloride ion has, at any concentration, the same mobility in all univalent chlorides. In this expression, Λ_1, Λ_2, γ_1, γ_2, n_1, n_2 denote respectively the equivalent conductivities, the degrees of ionisation of the two chlorides and the transport numbers (n) of Cl^- in the two solutions. This expression may be easily obtained as follows :—

The original expression of Arrhenius for the equivalent conductivity is—

$$\Lambda = F\gamma(U + V)$$

where U and V are the mobilities of the cation and anion (Cl^-) of the salt, strictly at the dilution in question. The transport number n of $Cl^- = V/(U + V)$. Hence $n\Lambda = F\gamma V$. In the case of Cl^- in KCl this is written with the suffix ($_1$), *i.e.* $n_1\Lambda_1 = F\gamma_1 V$, and for HCl at the same total concentration we write $n_2\Lambda_2 = F\gamma_2 V$, the same value V being assumed in both cases. Hence $n_2\Lambda_2/n_1\Lambda_1 = \gamma_2/\gamma_1$, as stated above. This ratio is given in the final column of the following table. The n_1, Λ_1, and γ_1 refer throughout to KCl, which is taken as a standard of comparison. $\Lambda_{0\cdot1}$, $\Lambda_{0\cdot01}$, and Λ_∞ denote the equivalent conductivities of the various chloride solutions at 0·1N, 0·01N, and at infinite dilution.

The product $\Lambda \times n_{Cl}$ may be conveniently termed the "equivalent conductivity of the chloride ion constituent" of the salt in question, being equal to $F\gamma V$. The constancy of this quantity (*cf.* fifth col. of the following table) as well as the constancy of the values in the last column is evident.

"This constancy of the equivalent conductivity of the chloride ion constituent at any given concentration does not, however, show whether

0·1N *Solutions.*

Chloride.	$\Lambda_{0\cdot1}$.	$\Lambda_{0\cdot1}/\Lambda_{\infty}$.	n_{Cl}.	$n_{Cl} \times \Lambda_{0\cdot1}$.	$\gamma_2/\gamma_{1(KCl.)}$.
HCl	351·4	0·925	0·1612	56·7	0·996
KCl	112·0	0·862	0·508	56·9	1·000
NaCl	92·0	0·844	0·617	56·8	0·998
LiCl	82·3	0·833	0·685	56·4	0·992
CrCl	113·4	0·850	0·500	56·7	0·996

0·01N *Solutions.*

Chloride.	$\Lambda_{0\cdot01}$.	$\Lambda_{0\cdot1}/\Lambda_{\infty}$.	n_{Cl}.	$n_{Cl} \times \Lambda_{0\cdot01}$.	$\gamma_2/\gamma_{1(KCl.)}$.
HCl	369·3	0·972	0·167	61·67	1·004
KCl	122·4	0·942	0·502	61·44	1·000
NaCl	101·98	0·936	0·603	61·44	1·000
LiCl	91·97	0·931	0·668	61·43	0·9998

the decrease of it with increasing concentration is due to decrease in the ionisation of the chloride, or to decrease in the mobility of the Cl^-, or to both of these effects. Since it is probable, in view of the above results, that the ionisation is the same in different chloride solutions at any given concentration, it is almost certain that the divergence of the conductivity ratio Λ/Λ_{∞} of HCl from that of the other chlorides, and the corresponding divergence in the change of the equivalent conductivity of the hydrogen ion constituent with the concentration from that of the other constituents, are really due to a considerable change with the concentration of the equivalent conductivity or the mobility of the hydrogen ion itself. And also, since differences in the variation of the mobilities of the ions are thus demonstrated, it is very probable that actual variations of larger magnitude than these occur with increasing concentration in the mobility of all ions."

We now pass to a consideration of ion activities.

"The preceding considerations which are based on the kinetic phenomenon of conductivity cannot, from their very nature, lead directly to a determination of the activity or effective concentration of ions, that is, to a determination of the concentrations which must be assigned to the ions in order that their actual mass action and other thermodynamic effects may be expressed by the familiar laws of perfect solutes. The conclusions reached in the preceding paragraphs do, however, much increase the probability of a simple hypothesis which greatly assists in determining the probable values of the activities of the separate ions; namely, the fact, demonstrated above, that the equivalent conductivity of the chloride ion constituent at any given concentration is *independent* of the cation constituent, and the strong presumption that the concentration and mobility of the chloride ion is the same at any given concentration in the solutions of univalent chlorides raises

the further presumption that the *activity* of the chloride ion, at any given concentration, is also *independent* of the cation associated with it.

"This hypothesis differs from that employed up to the present time in computing activities. It has been commonly assumed that the cation and the anion of the substance have *equal* activities in the same solution, even in the case of hydrogen ion and of chloride ion in hydrochloric acid." This conclusion MacInnes does not regard as correct, except in the case of KCl. He assumes, therefore, that these two ions, K^+ and Cl^-, which have nearly the same weight and mobility, have sensibly the same *activity* in a solution of the salt.

To show how on this basis the activity of a single ion, say the hydrogen ion, can be computed we have to consider cells of two types A and B, *viz.* cells without and cells with transport:—

$$\left.\begin{array}{l} \mathrm{Ag} \mid \mathrm{AgCl,\ KCl}(c_1) \mid \underset{\text{amalgam}}{\mathrm{K}_x\mathrm{Hg}} \mid \mathrm{KCl}(c_2),\ \mathrm{AgCl} \mid \mathrm{Ag} \\ \mathrm{Ag} \mid \mathrm{AgCl,\ HCl}(c_1) \mid \underset{1\ \text{atmos.}}{\mathrm{H}_2} \mid \mathrm{HCl}(c_2),\ \mathrm{AgCl} \mid \mathrm{Ag} \end{array}\right\} \text{A}$$

$$\left.\begin{array}{l} \mathrm{Ag} \mid \mathrm{AgCl,\ KCl}(c_1) \,\vdots\, \mathrm{KCl}(c_2),\ \mathrm{AgCl} \mid \mathrm{Ag} \\ \mathrm{Ag} \mid \mathrm{AgCl,\ HCl}(c_1) \,\vdots\, \mathrm{HCl}(c_2),\ \mathrm{AgCl} \mid \mathrm{Ag} \end{array}\right\} \text{B}$$

The electromotive forces E_A and E_B of cells of these two types are given by the following expressions, in which a_1^+, a_1^-, a_2^+, a_2^-, denote respectively the activities of the positive and negative ions at the two (salt) concentrations c_1 and c_2, and n is the transport number of the cation; (the cation in this case because the electrodes are reversible with respect to the anion):—

$$E_A = \frac{RT}{F}\log_e a_1^+ a_1^- / a_2^+ a_2^-$$

$$E_B = \frac{nRT}{F}\log_e a_1^+ a_1^- / a_2^+ a_2^-.$$

From the e.m.f. values for the potassium chloride concentration cells of both types, by putting $a_1^+ = a_1^-$, and $a_2^+ = a_2^-$, we can find the ratio a_1^-/a_2^- for the *chloride ion* at salt concentrations c_1 and c_2. Then from the e.m.f. data for the hydrochloric acid cells containing acid at the *same* concentrations, c_1 and c_2, as those of the KCl solutions, we can find, by substituting the above value of a_1^-/a_2^- in the appropriate equation, the value of a_1^+/a_2^+ for the *hydrogen* ion. Further, at very great dilution we again assume that the value of α becomes identical with γ. Since we have already concluded that γ is the same for HCl as it is for KCl, it follows that the value attributed to α for KCl at great dilution is the same as the value to be attributed to HCl likewise at great dilution. With this as a starting point, and knowing the value of the ratio

a_1^+/a_2^+ for the hydrogen ion at other dilutions from the e.m.f. data, as indicated above, we are able to calculate the absolute values of the activity of hydrogen ion at any concentration of HCl. The values so computed by MacInnes are given in the following table—

Cumulates of KCl or HCl.	Activities (*a*).		Activity Coefficients (*a*).	
	K^+ or Cl^-.	H^+.	K^+ or Cl^-.	H^+.
0·001665	(0·001627)	(0·001627)	0·976	0·976
0·003330	0·003140	0·003205	0·935	0·972
0·00500	0·004588	0·004750	0·918	0·949
0·00666	0·006215	0·006247	(0·932)	0·937
0·0100	0·008785	0·009257	0·878	0·925
0·01666	0·01441	0·01526	0·864	0·915
0·03333	0·02750	0·02945	0·825	0·883
0·05000	0·0396	0·0434	0·792	0·869
0·100	0·0732	0·0854	0·732	0·854

More recently Chow (*Journ. Amer. Chem. Soc.*, **42**, 497 (1920)) has measured the e.m.f. of cells containing both HCl and KCl simultaneously, the cells being of the type—

$$H_2\ (1\ \text{atmos.}) \;\Big|\; \begin{matrix} HCl\,c_1 \\ KCl\,c_2 \end{matrix},\ Hg_2Cl_2 \;\Big|\; Hg$$

in which the separate concentrations c_1 and c_2 are varied, but always in such a way as to keep their sum at 0.1N. The results obtained go to show that the activity of the chloride ions in solutions of *mixed* univalent chlorides is independent of the nature of the cations present, which is in agreement with the conclusion arrived at by MacInnes.

Résumé.

We have now considered in some detail the nature of the problems, only partially solved, which present themselves in attempting to deal with degrees of ionisation and activity coefficients of ions in dilute solutions of electrolytes. As regards the numerical differences between these two quantities it will be recalled that the activity coefficient is in general (over a wide range of concentration) a smaller term than the degree of ionisation. In this connection Tolman has made the following suggestion (quoted from a private communication from Dr. MacInnes) "If we could see into a salt solution with a super-ultramicroscope it would be difficult to tell whether a given molecule were actually dissociated or not, as the molecules would be in all possible stages between complete dissociation and no dissociation. It is possible, for instance, that an ion but slightly removed from its parent molecule might be able to affect the conductivity whereas it might not be able to affect the e.m.f. at an electrode, and thus determinations of ionisation by conductivity would be expected to differ from those (*i.e.* be numerically greater than those) obtained from e.m.f. or freezing point determinations." This has some-

thing in common with the idea first suggested by A. A. Noyes (*cf. Journ. Amer. Chem. Soc.*, **30**, 335 (1908), but more recently withdrawn) that "ions are partially united, as a result solely of their electrical attractions, into loosely bound molecules, which differ fundamentally from the stable molecules formed as a result of chemical affinity in accordance with the law of mass action".

It must be emphasised that we have no real proof that the conductivity ratio, Λ_v/Λ_∞, actually represents the degree of ionisation in any case. It has been suggested that the change in the conductivity ratio with concentration has its origin not in a true alteration in the degree of ionisation but in a change in the mobility of the ions with change in concentration. The doubt regarding the real significance of the conductivity ratio is rendered greater by the recent introduction of the hypothesis that strong electrolytes are completely ionised at all concentrations which can be regarded as dilute (*cf.* Milner, *Phil. Mag.*, **35**, 214, 354 (1918); Ghosh, *Trans. Chem Soc.*, **113**, 449, 627 (1918); Bjerrum, *Zeitsch. Elektrochem.*, **24**, 321 (1918); Sutherland, *Phil. Mag.* [6], **14**, 3 (1907)). This assumption cannot be true of course for the more concentrated solutions in which the vapour pressure of the undissociated molecules of the electrolyte (*e.g.* the halogen acids) is measurable. Reviewing the present state of knowledge (1920) in regard to this point Noyes and MacInnes (*loc. cit.*) conclude that, "it seems advisable to adopt for the present the hypothesis that such substances [strong electrolytes] are completely ionised and to attribute the decrease in the conductivity ratio wholly to a decrease of ionic mobility, and the change in the activity coefficient to some unknown effect of a physical nature".

As regards this "unknown effect" which enters into the idea of activity and activity coefficient, the present writer ventures to suggest that it is ultimately to be attributed to a new factor involved in the concept of activity, namely, the radiation density of the type or frequency characteristic of the molecular or ionic species considered, in virtue of which such species exhibit chemical reactivity. The idea that radiation—belonging to the *far* infra-red region—plays a fundamental part in connection with the *average* internal energy of substances (the variation of which with temperature we measure as atomic or molecular heat) has been recognised since Einstein, in 1907, first attempted to apply the Quantum Theory to the atomic heats of solids. On the other hand it has long been recognised that more specifically "chemical" changes can be brought about by radiation of short wave length, *viz.* the well-known photochemical reactions. It is a reasonable extension of the idea to regard the radiation of the short infra-red region, say, 1μ to 10μ, as the origin of ordinary or thermal reactions, including ionisation, which occur at room temperature in virtue of the temperature of the system. To give some degree of precision to this idea it is necessary to treat thermal reactions from the quantum standpoint. This was first done by the writer (*Trans. Chem. Soc.*, 1914 and onwards). This mode of treatment cannot be discussed further in this place; it is referred to in Vol. III., which deals with the Quantum Theory in its

general physico-chemical aspects. It may be pointed out, however, that this way of regarding activity involves a restatement of the law of mass action, the reactivity of a species (which we may identify with G. N. Lewis' activity term) depends not simply upon—and indeed in certain cases not mainly upon—the mere concentration of an individual, but simultaneously upon the density of the radiation characteristic of the substance and absorbable by it.[1]

This product of concentration into radiation density gives a more complex quantity, but, at the same time, probably a more accurate measure of the concept of active mass than is expressed in the classic concept of concentration alone. This new measure of active mass is of significance not only for "stoicheiometric" reactions, but also for catalytic reactions, in which the catalyst may act in a stoicheiometric manner (expressible, in so far as *material* change is concerned, by the ordinary stoicheiometric equations), and also for catalytic effects such as the influence of the solvent (or additions to the solvent) which cannot be expressed "stoicheiometrically," since the effect has its origin in a physical (radiational) mechanism.

With this suggestion in mind we are at once led to widen the scope of our present considerations. We proceed to give a short account of certain results obtained by Harned (*Journ. Amer. Chem. Soc.*, **40**, 1461 (1918)) in connection with catalysis by salts, and likewise the conclusions arrived at by McBain and Kam (*Trans. Chem. Soc.*, **115**, 1332 (1919)) in connection with the apparent effect of neutral salts upon the degree of ionisation of a weak electrolyte.

The Activities of the Ions in Neutral Salt Catalysis.

We shall here consider the case most fully dealt with by Harned (*loc. cit.*), namely, the decomposition of H_2O_2 by the iodide ion, produced by the ionisation of KI, in presence of such salts as KCl and NaCl. Such salts increase the unimolecular velocity constant of decomposition of hydrogen peroxide, the catalytic effect being attributed by Harned to the Cl^- of the added salt. It is, perhaps, more justifiable not to attempt to differentiate between the catalytic effects of the added cation and anion, more especially as the numerical results are referred to the "average" activity of the added ions, that is to the quantity ($\sqrt{a^+a^-}$), and not to the activity of the chloride ion *per se*, which, in view of MacInnes' work already referred to, would be expected to possess the same catalytic effect whether the added salt contains potassium or sodium or any other univalent cation. From known e.m.f. results the "average" ionic activity can be obtained. Making use of such values Harned shows that the observed velocity constant of decomposition is proportional to the activities as is set forth in the following table:—

[1] A non-mathematical treatment of this concept of reactivity or activity is given by the writer in *Scientia*, **25**, June (1919).

Concentration of KI = 0·03N.

Molar Concentration of KCl or NaCl.	k_1 (Unimolecular Velocity Constant of Decomposition $\times 10^2$) in presence of KCl.	k_2 (Unimolecular Velocity Constant $\times 10^2$) in presence of NaCl.	"Average" Activity of KCl Ions, $a_1 = \sqrt{a_1^+ \times a_1^-}$	"Average" Activity of NaCl Ions, $a_2 = \sqrt{a_2^+ \times a_2^-}$	$\frac{k_1 \times 10^2}{a_1}$	$\frac{k_2 \times 10^2}{a_2}$
0·000	4·18	4·18	—	—	—	—
0·500	4·31	4·45	0·305	0·311	14·14	14·20
1·000	4·45	4·79	0·584	0·628	7·63	7·65
1·500	4·57	5·20	0·860	1·000	5·32	5·40
2·000	4·70	5·64	1·150	1·397	4·08	4·04
2·500	4·85	6·12	1·433	1·815	3·38	3·32
	Concentration of KI = 0·02N.					
0·000	2·75	2·75	—	—	—	—
0·500	2·84	2·93	0·305	0·311	9·31	9·40
1·000	2·93	3·17	0·584	0·628	5·02	5·05
1·500	3·02	3·44	0·860	1·000	3·51	3·44
2·000	3·11	3·77	1·150	1·397	2·70	2·70
2·500	3·19	4·19	1·433	1·815	2·22	2·25

Similar relationships were obtained from a consideration of Rivett's data upon the conversion of acetochloranilide into p.-chloroacetanilide. These results, as Harned points out, at once raise the question of the reality of the catalytic effect attributed to the undissociated molecules of the catalyst, a view already discussed in Vol. I. That the problem is not simple is evidenced at once by the fact that although k_1/a_1 is equal to k_2/a_2 at any given concentration of the added salts, this ratio is not independent of the total concentration of the added salt. Further, if we consider a point not discussed by Harned, *viz.* the increase Δk in the velocity constant brought about by increasing the concentration of the added neutral salt, we obtain values which differ according to the nature of the neutral salt, and apparently in the case of NaCl the value of $\Delta k/a_2$ is not constant. These results are given in the following table:—

Concentration of Salt.	Δk in presence of NaCl.	Δk in presence of KCl.	$\Delta k/a_1$ KCl.	$\Delta k/a_2$ NaCl.
0·500	0·27	0·13	0·43	0·87
1·000	0·61	0·27	0·46	0·97
1·500	1·02	0·39	0·45	1·02
2·000	1·46	0·52	0·45	1·05
2·500	1·94	0·67	0·46	1·07

There is evidently an effect entering into the phenomenon in addition to that directly due to the activity of the ions. We naturally think of the solvent-displacement effect discussed in Vol. I. Such displacement or removal of solvent may be brought about by the mere act of adding the neutral salt and also by the hydration which the neutral

salt undergoes. The general significance of hydration in connection with reaction velocity is considered by Harned. It has been suggested that activity itself is related to hydration, but whilst this is undoubtedly true they are scarcely to be regarded as related to one another as cause and effect. The problems referred to obviously require a great deal further investigation.

The Influence of Neutral Salts upon the Activities of Ions and Molecules.

An important conclusion has been arrived at by McBain and Kam (*loc. cit.*) in a paper with the following self-explanatory title: "The effect of salts on the vapour pressure and degree of dissociation of acetic acid in solution. An experimental refutation of the hypothesis that neutral salts increase the dissociation constants of weak acids and bases."

We are here considering the behaviour of a weak, not of a strong, electrolyte. Owing to the fact that the law of mass action as ordinarily expressed, that is, expressed in concentration terms as given by the conductivity method, applies satisfactorily to such cases, the necessity of introducing the idea of activities even here does not appear to have been appreciated until quite recently.

It has long been known that the potential of the hydrogen electrode in an aqueous solution of a weak acid, say, acetic acid, corresponds apparently to a *higher* concentration of H^+ when some neutral salt, *e.g.* NaCl, is added to the solution than it does in the absence of the salt. This was usually interpreted as meaning a real increase in the ionisation, and therefore an increase in the ionisation constant or strength of the weak electrolyte, brought about by this "neutral salt action". As McBain and Kam point out, however, the electric potential of the hydrogen electrode measures the product of the chemical potential and the concentration of the hydrogen ion. (This is equivalent to saying that it measures the activity and not merely the concentration of the ions, the value obtained corresponding, as we have already shown, to the so-called average activity $\sqrt{a^+a^-}$ of either ion.) Instead of assuming that the increase in this product (*i.e.* chemical potential × concentration) is due to increase in concentration, McBain and Kam submit experimental evidence that it is the chemical potential which has been increased by the neutral salt. This evidence will be given a little later. The point of view is interesting as indicating the independence of the two factors concerned. On the radiation hypothesis already referred to we would use the term density of the radiation or radiational field in place of the thermodynamic term, chemical potential. "If the concentration of the hydrogen ion has remained unaltered, but its chemical potential or reactivity has been increased, it is necessary for the continuance of equilibrium that the chemical potential or reactivity of the undissociated molecules of acetic acid should likewise have been increased. Such increase in reactivity on the part of the molecules must, if it exists, be accompanied by a parallel increase in the partial

pressure of acetic acid in the vapour phase." This is open to direct test, and McBain and Kam find that a remarkable increase in activity of the molecules is actually exhibited, "fully accounting for the electrometric data observed" in connection with the ions. In other words the increase in the activity of the undissociated molecules, due to the presence of the neutral salt just balances the increase in activity of the ions due to the same cause, with the result that the dissociation constant and the degree of ionisation remain unaltered.

The experimental method employed for the determination of the partial pressure of acetic acid molecules in the vapour phase consisted in the distillation of aqueous solutions of acetic acid, with and without the addition of various salts, with corresponding analyses of both liquid and (condensed) vapour phases. The details of the method and the mode of calculation will be found in the original paper.

It was found that many salts increase the partial vapour pressure of undissociated acetic acid by quite measurable amounts. Thus, in the case of 2·3 normal NaCl the increase in partial pressure of the acetic amounts to as much as 63 per cent. Sodium chloride, in fact, has a greater influence than the other salts investigated, namely, KCl, KCNS, Na_2SO_4, KNO_3, LiCl, $NaCH_3CO_2$. This is suggestive in the light of the results obtained by Harned. It is evident that these salts are behaving towards the weak electrolyte in much the same way as they do towards strong electrolytes. McBain and Kam find that sodium acetate is practically without effect. In general the activation effect is independent of the concentration of the acetic acid. This at once suggests an environmental influence of a physical nature, such as might be identified with radiation density.

Of the salts examined, sodium sulphate is exceptional in its behaviour in that up to about 0·35N there is a very slight negative effect, becoming positive above this concentration. This behaviour of sodium sulphate is important in view of certain results obtained by Thomas and Miss Baldwin (*Journ. Amer. Chem. Soc.*, **41**, 1901 (1919)) referred to briefly later.

McBain and Kam point out that "it is well known that there is a general qualitative similarity between the effect of neutral salts on such various phenomena as solubility of gases and non-electrolytes, surface tension, compressibility, maximum density of water, viscosity, dielectric capacity, imbibition and gelatinisation of gels, and increase or decrease of rate of catalysis."

Returning to the specific point with which we began, namely the question as to whether the presence of neutral salts alters the degree of ionisation of a weak electrolyte it is important to show as quantitatively as possible that the alteration is either nil or practically so.

McBain and Kam state that in the case of a 0·2N solution of acetic acid, the reactivity of the undissociated molecules of the acid is increased by 5·5 per cent. in the presence of 0·2N NaCl. Walpole's measurements of the e.m.f. in this case showed that the apparent hydrogen ion increase amounted to 7 to 8 per cent. "These two effects,

namely, 5 per cent. and 7 to 8 per cent. are equal within the experimental, and thus the effect on the dissociation constant cancels out, and leaves that constant unchanged by the presence of the salt."

In the above connection it may be mentioned that it has been found in the writer's laboratory that the presence of sucrose likewise increases the apparent concentration of hydrogen ion (actually the activity) in H_2SO_4 solutions, as indicated by e.m.f. measurements. This constitutes a considerable extension of the field here considered, since the effect referred to can be equally well brought about by an electrolyte as by a non-electrolyte. It is possible that the sucrose acts mainly by "displacing" the solvent (water) thereby bringing about a new physical environment. Further, in the case of concentrated solutions of *weak* electrolytes, the Ostwald constant, as ordinarily expressed in *concentration* terms, may alter, owing to the lack of the proportionality between activity and concentration which exists obviously in dilute solutions of such substances. There is obviously some underlying cause for all these phenomena—probably of a physical nature such as that already suggested.

The Behaviour of Chromium Chloride Solutions in presence of added Neutral Salts.

In connection with the chrome tanning of leather it has been found in technical practice that by the addition of neutral salts it is possible to use more basic chrome liquors. The added salt prevents the precipitation of hydrated chromium oxide. This phenomen has been regarded as due to an actual increase in hydrogen ion concentration. It is much more probable, however, that we are dealing with an increase of activity rather than an increase of mere concentration. Instead of dealing with the complex system presented in the tanning bath we shall refer briefly to the results obtained by Thomas and Miss Baldwin (*loc. cit.*) in the chemically better defined case of a solution of chromium chloride.

The added salts were the chlorides of lithium, sodium, potassium, ammonium and barium. From e.m.f. measurements it is inferred that all these apparently raise the hydrogen ion concentration produced by the hydrolysis of the chromium salt. The barium chloride is the most effective, then lithium chloride, then sodium chloride, and lastly potassium and ammonium chlorides. Undoubtedly these follow approximately the degrees of hydration, *i.e.* the solvent-displacement-effect is entering into the problem. Even in the case of chromium choride a complication enters, namely, the so-called "ageing" of the solution, no doubt connected with the colloidal nature of the hydrolytic products. To obtain still more unequivocal results, solutions of HCl and H_2SO_4 of the same H^+ concentration as the chromium chloride and chromium sulphate were next examined. In the case of H_2SO_4 (0·0005N) it was found that the addition of NaCl and of NH_4Cl increased the apparent concentration of H^+, whilst NH_4SO_4 decreased it somewhat and Na_2SO_4 decreased it very markedly. In the case of HCl (0.004N)

the apparent increase in the H^+ concentration produced by the addition of the chlorides already mentioned was closely analogous to that found in the case of chromium chloride. On the other hand, NH_4SO_4 apparently decreased the H^+ most markedly, Na_2SO_4 less markedly, and $MgSO_4$ first apparently diminished the H^+ and later increased it. The results referred to here are rendered more difficult to interpret owing to the probability of double decomposition of the sulphates with the hydrochloric acid and the chlorides with the sulphuric acid. Experiments with HCl to which $MgCl_2$ was added showed that this salt markedly increases the apparent H^+ concentration. The sulphates are therefore sharply distinguished from the chlorides in their behaviour. What is really measured in these cases, as Thomas and Miss Baldwin themselves imply, is the average activity of the H^+ and the anion of the acid. The behaviour is analogous to that found by McBain and Kam in the case of addition of a salt to a weak acid.

CHAPTER IX.

Chemical equilibrium in homogeneous systems—Concentrated solutions.

Experimental Results Obtained in the Measurement of High Osmotic Pressures.

In Vol. I. it was pointed out that in the case of *dilute solutions* of non-electrolytes, the experimental work of Morse and Frazer and their collaborators had shown that the osmotic pressure actually measured is identical within the limits of experimental error, with the gas pressure as predicted by the van 't Hoff formula. That is, at constant temperature T the osmotic pressure is strictly a linear function of the concentration, *i.e.* $P = RTC$. When the solutions begin to be moderately concentrated, however, this linear relation is gradually departed from. Measurements at high concentration are extremely difficult to make, owing to the difficulty of obtaining membranes sufficiently stout, even when deposited upon porcelain tubes, to stand the great difference of pressure. Within recent years, however, this has been accomplished in the classic work of the Earl of Berkeley and Mr. E. G. J. Hartley (*Phil. Trans.*, **206** A, 481, 1906). Their method of measuring P was to determine the "equilibrium pressure," that is the pressure which must be applied to the *solution* to bring about a state of equilibrium between it and the solvent, so that no solvent, *i.e.* water, passes in either direction as a whole when the solution and solvent are separated by a semi-permeable membrane. In these measurements the solvent was under the pressure of the atmosphere. The pressure applied to the solution so that there is no movement of the solvent is the sum of the "equilibrium pressure," *i.e.* P_1 plus the pressure exerted on the solvent, *i.e.* the atmosphere. The details of the apparatus and method of working will be found in the paper referred to. The following are a few of the results obtained with pure cane sugar. The temperature of measurement is 0° C. The *concentration* is expressed as weight of sugar in grams in 1 liter of *solution* prepared at 15° C. The solvent is at 1 atmosphere pressure.

Osmotic Pressure Measured at 0° C.

180·1 grams per liter	P = 13·95 atmospheres
300·2 ,, ,,	P = 26·77 ,,
420·3 ,, ,,	P = 43·97 ,,
540·4 ,, ,,	P = 67·51 ,,
660·5 ,, ,,	P = 100·78 ,,
750·6 ,, ,,	P = 133·74 ,,

These results give some idea of the enormous values actually reached in concentrated solutions. The curve (Fig. 27) shows the osmotic pressure plotted against concentration, so as to show the departure of the P values from the simple linear relation, which holds in dilute solutions. The straight line is drawn on the usual assumption that 1 gram molecular weight of solute per liter (solution) should give an osmotic pressure of 22·4 atmospheres.

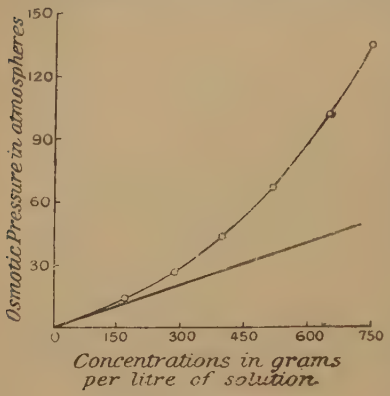


FIG. 27.

Other sugars were also employed, and in later papers an account is given of similar very accurate measurements both of osmotic pressure and lowering of vapour pressure, due to calcium ferrocyanide in water, this salt being a very soluble one, and one which at the same time is practically stopped by the copper-ferrocyanide semi-permeable membrane (Earl of Berkeley, E. G. J. Hartley, and C. V. Burton, *Phil. Trans.*, **209** A, 177, 1909. Dilute solutions of the same solute were also investigated by the Earl of Berkeley, E. G. J. Hartley, and J. Stephenson, *ibid.*, p. 319.) For details the reader is again referred to the original papers. The object of the work referred to was to test Porter's equation. This equation will be taken later.

THEORETICAL TREATMENT OF THE OSMOTIC PRESSURE OF CONCENTRATED SOLUTIONS.

Sackur's Equation of State for Solutions of any Concentration.

In view of the fact that the simple expression PV = RT breaks down for concentrated solutions, it is natural to expect that attempts would be made to account for the behaviour, by applications of gas equations such as that of van der Waals, *viz.* $\left(p + \frac{a}{v_2}\right)(v - b) = \mathrm{RT}$. This has been attempted by a fairly large number of workers, with only partial success, however. To get an idea of this method of treatment the reader should consult the paper of O. Stern (*Zeitsch. physik. Chem.*, **81**, 441, 1912).[1] Apart from the fact that the van der Waals equation is not a *very* accurate one for compressed, *i.e.* concentrated, gases, and therefore may be expected to be similarly inexact for solutions, it will be at once evident that the "constants" a and b in the case of solutions are much more complex quantities than in the case of a single gas,

[1] For a criticism of Stern's paper see J. J. van Laar (*Zeitsch. physik. Chem.*, 82 223, 1913).

owing to the presence of different kinds of molecules, namely, those of the solvent and those of the solute. The molecular attractions which are taken account of by the term a are due to—

(1) attractions between the molecules of solute for one another, and

(2) attractions between the molecules of solute and the molecules of solvent.

Rather remarkably, however, O. Sackur (*Zeitsch. physik. Chem.*, **70**, 477, 1910) has discovered that a *simplified* form of van der Waals' equation actually holds good with considerable accuracy up to very high concentrations. The expression is—

$$P(V - b) = RT$$

where P is the osmotic pressure,

V = the volume of solution in which 1 mole of solute is dissolved,

R = gas constant 1·985 calories per degree or 0·082 liter atmospheres,

T = absolute temperature.

It is important to note the definition of V, *i.e.* volume of solution, for in concentrated solution, owing to changes in volume (contraction or expansion) due to solute, one cannot assume that 1 liter of solution can be produced by adding the required mass of solute to 1 liter of solvent. In the following table are given some of the data used by Sackur to test his equation in the domain of concentrated solutions.

Solvent: *Water.* Solute: *Glucose at* 0° *C.* (Measurements of Berkeley and Hartley.)

V.	P in Atmospheres.	PV (Obs.).	PV Calculated by Sackur's Equation.
1·805	13·2	23·9	24·4
0·903	29·2	26·3	26·8
0·565	53·2	30·0	30·4
0·402	87·8	35·2	35·5
0·328	121·2	41·0	40·6

Solvet: *Water.* Solute: *Acetamide.* (Measurements of P obtained indirectly, from freezing-point determinations by Jones and Getman, *Amer. Chem. Journ.* **32**, 308, 1904.)

P Atmospheres.	PV Observed.	PV Calculated by Sackur's Equation.
23·5	23·5	23·7
49·6	24·8	25·3
79·6	26·5	27·0
114	28·5	29·0
148·5	29·7	31·0
203	33·8	34·1
272	38·9	38·2
347	43·4	42·5
445	49·4	48·2

Sackur found that the b term of the equation showed, in general, an increase, as solutes of higher molecular weight were employed in the same solvent. Further, Sackur found that b was very sensitive to temperature. Thus for glucose at 0° C. $b = 0{\cdot}16$, at 22° C. $b = 0{\cdot}093$. He considers that this is due to the hydration of solute molecules, the degree of hydration varying rapidly with temperature. The applicability of the simple equation $P(V - b) = RT$ shows that van der Waals' constant a, which takes account of molecular attractions, can be neglected up to extremely high concentrations. Sackur attempts to make this appear at least plausible on the following grounds. The apparent lessening of the pressure (directed outwards) due to the attraction of the molecules, inwards, is naturally only effective at the surfaces of the compressed gases, or pure liquids (as these attractive forces balance one another in the bulk of the gas or liquid). In solutions, however, there exist, besides attraction between the solute molecules themselves, attractions also between the solute molecules and the solvent molecules, and the latter, according to Sackur, "are probably much the greater". In the process of performing osmotic work, *i.e.* in the process of diluting a solution by the addition of some solvent, some work is done in drawing the solute molecules apart from one another, *i.e.* work *against* the first type of attraction; while, on the other hand, the process of dilution is actually aided by the attraction between the solvent and solute molecules. Since these two effects are mutually opposed, it is reasonable to expect that the total attraction effects in solution will only become noticeable at much higher concentration than in the gaseous state itself (Bredig, *Zeitsch. physik. Chem.*, **4**, 44, 1889).

Connection Between the Osmotic Pressure of Concentrated Solutions and the Relative Lowering of Vapour Pressure.

This problem has likewise been the subject of much theoretical investigation, generally of a very complicated kind. A full discussion will not be attempted here. For further information the reader is referred to the treatment of the subject and papers cited by Nernst in his textbook (English edition, p. 155 *seq.*), notably those of McEwan (*Zeitsch. physik. Chem.*, **14**, 409, 1894), Dieterici (*Wied. Annalen*, **42**, 513, 1891; **50**, 47, 1893; **52**, 263, 1894), and also Noyes (*Zeitsch. physik. Chem.*, **35**, 707, 1900).

In the present instance we shall restrict ourselves to two lines of treatment, namely, that followed by Sackur in his book *Lehrbuch der Thermochemie und Thermodynamik*, p. 200 *seq.*, and also the more general comprehensive theory of osmotic pressure and lowering of vapour pressure as worked out by A. W. Porter (Part I., *Proc. Roy. Soc.*, **79** A, 519, 1907; Part II., *Proc. Roy. Soc.*, **80** A, 457, 1908).

Sackur's modification of the Equation connecting Lowering of Vapour Pressure and the Osmotic Pressure for Solutions of any Concentration.

In dealing with the lowering of vapour pressure of dilute solutions, the following formula for the osmotic pressure P was deduced :—

$$P = \frac{dx}{dv} RT \log \frac{p_0}{p}.$$

The vapour was supposed to behave approximately as a perfect gas, and further the term $\frac{dx}{dv}$ was taken to be the density of the solvent which was considered to be sensibly the same as that of the solution, *i.e.* the solution was so dilute that on adding a volume of solvent dv the volume of the solution increased exactly by this amount. If, however, the solution is concentrated, addition of the solvent (volume dv) will not cause simply this increase in the volume of the solution. The actual increase may be either less or greater than dv. The term $\frac{dx}{dv}$ as it appears in the thermodynamic cycle followed, must be replaced by a slightly more complicated function in the case of concentrated solutions.

Let us denote by ρ the density in grams per cubic centimeter of a given solution, which contains 1 mole of solute and x moles of solvent (reckoned as simple molecules), in V liters of solution. If M is the molecular weight of the dissolved solute and M_0 the molecular weight of the solvent, then we can write—

$$\frac{M + xM_0}{V1000} = \rho$$

and hence

$$dx = \frac{1000}{M_0}(\rho dV + V d\rho)$$

or

$$\frac{dx}{dV} = \frac{1000}{M_0}\left(\rho + V\frac{d\rho}{dV}\right).$$

If c is the concentration of the solute in moles per liter (of solution) then $c = \frac{1}{V}$, and hence—

$$\frac{dx}{dV} = \frac{1000}{M_0}\left(\rho - c\frac{d\rho}{dc}\right).$$

Hence the expression for the osmotic pressure may be written—

$$P = \frac{1000}{M_0}\left(\rho - c\frac{d\rho}{dc}\right)RT \log \frac{p_0}{p}.$$

For a dilute solution c is nearly zero, and ρ becomes ρ_0, the density of the solvent. That is—

$$P = \frac{1000}{M_0}\rho_0 RT \log \frac{p_0}{p}$$

which is the van't Hoff equation previously deduced with a slight alteration in the concentration units included in the term $\frac{1000}{M_0}$. Sackur has tested the above relation for concentrated solutions; the only investigation hitherto carried out which afforded sufficient data to calculate the expression completely being that of the Earl of Berkeley and Hartley (*loc. cit.*) on solutions of calcium ferrocyanide. In the following table taken from Sackur's textbook, is given the comparison of the found and calculated results.

VAPOUR PRESSURE AND OSMOTIC PRESSURE OF CONCENTRATED CALCIUM FERROCYANIDE SOLUTIONS AT 0° C.

Grams of $Ca_2Fe(CN)_6$ in 1000 Grams of Water.	ρ.	c in Moles per Liter.	$\frac{d\rho}{dc}$.	$\frac{p_0}{p}$ Found.	P Atmosphere Calculated by Sackur.	P Atmospheres Found.
313·9	1·224	1·00	0·195	1·033	40·7	41·22
395·0	1·270	1·23	0·190	1·057	70·8	70·84
428·9	1·287	1·32	0·183	1·070	86·2	87·09
472·2	1·309	1·44	0·181	1·092	114·0	112·84
499·7	1·322	1·51	—	1·107	131·0	130·66

As Sackur points out, this relatively simple formula gives very satisfactory agreement between observed and calculated values. Berkeley and Hartley have deduced a more complicated formula which will be referred to in Porter's theory (*vide infra*), in which compressibility of the solution was allowed for as well. In the above formula the solution is treated as though incompressible, the change in density with concentration being alone allowed for. It must be remembered also that the vapour (of the solvent) has been treated as a perfect gas, and the solute has been treated as absolutely non-volatile.

Porter's Theory of Compressible Solutions of any Degree of Concentration.

In the following account, Prof. Porter's own words are employed practically throughout. It has been considered sufficient for the present purpose to restrict ourselves to the case in which solvent alone is volatile. The further case, where both solute and solvent are volatile, is given in Porter's second paper (*loc. cit.*). One point remains to be noted, namely, the emphasis which is laid in Porter's theory on the effect of hydrostatic pressure upon vapour pressure. It is a well-known experimental fact that if we add, say, an inert gas to a vessel containing a liquid and its saturated vapour, the increase in pressure in the vessel due to the inert gas, causes an increase in the actual pressure (partial pressure) of the saturated vapour. From the molecular standpoint one might regard the phenomenon as due to the increased number of

impacts by the gas molecules on the molecules of the liquid, whereby more molecules per unit surface area are capable of forming vapour, *i.e.* the vapour pressure rises. With this reference by the way we can now go on with Porter's paper.

"This paper is an attempt to make more complete the theory of solutions, at the same time maintaining as great simplicity of treatment as is possible without sacrificing precision. Renewed attention has been called to the subject, owing to the success of the experiments of the Earl of Berkeley and Mr. E. J. Hartley on the osmotic pressure of concentrated solutions of sugar. Diversity of opinion has existed in regard to the interpretation of these experiments, insufficient attention having been previously paid to the influence of the hydrostatic pressure of the pure solvent upon the value of the osmotic pressure. The principal advances made in this paper consist in simply demonstrating the influence of pressure upon osmotic pressure for *compressible* solutions and in including the effect of the variability of vapour pressure with hydrostatic pressure. The influences of accidental properties (such as the effects of gravitation) are excluded.

"*Summary of Notation.*

"The following is the notation employed. All the values are isothermal values.

Solution—

Hydrostatic pressure	p
Vapour pressure corresponding to hydrostatic pressure p	π_p
Vapour pressure when solution is in contact with its own vapour alone	π_π
Volume at hydrostatic pressure p	V_p
Reduction of volume when 1 gram of solvent escapes	s_p
Osmotic pressure for hydrostatic pressure p	P_p
" " " π_π	P_π

Solvent—

Pressure of solvent when solution is at pressure p	p_0
Corresponding vapour pressure	π_{0p_0}
Vapour pressure when hydrostatic pressure is that of its own vapour	π_{00}
Volume at hydrostatic pressure p_0	V_{0p_0}
" " " π_{00}	$V_{0\pi_0}$
Specific volume at hydrostatic pressure p_0	u_{p_0}
" " " " π_{00}	u_{π_0}

Vapour of Solvent—

Specific volume at pressure π_{00}	v_0
" " π_{p_0}	v_{p_0}
" " π_p	$v_{\pi p}$
" " π_π	v_π

A few special symbols are defined in the text.

"*Relation between Osmotic and Vapour Pressures.*

"The following isothermal cycle enables the above relation to be found. A large (practically infinite) quantity of a solution (unacted upon by any bodily field of force, such as gravity) is separated from a quantity of pure solvent by a semi-permeable membrane. *The solute is supposed to be involatile.* The solution is under a hydrostatic pressure p, while the solvent is under the hydrostatic pressure p_0 for which there will be equilibrium. It is not intended that either of these pressures shall be restricted to be the vapour pressure of the corresponding liquid.[1]

"(1) Transfer 1 gram of solvent from the solution to the solvent by moving the semi-permeable membrane to the left, in Fig. 28; the work done upon the system is—

$$P_p s_p - p_0(u_{p_0} - s_p).$$

"(2) Separate 1 gram of the pure solvent (at p_0) from the rest by partitioning off the lateral tube; change its pressure to π_{00} (by aid of

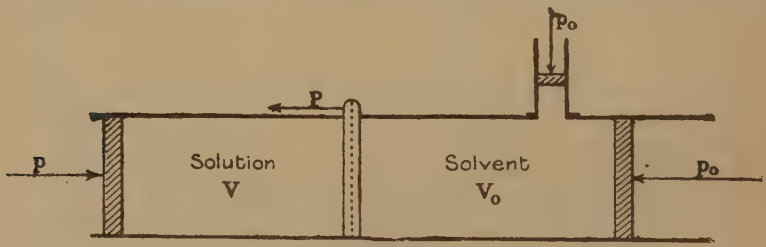


FIG. 28.

the lateral piston), so that it will be in equilibrium with its own vapour, and then evaporate it; the work done is—

$$-\int_{u_{p_0}}^{u_{\pi_0}} p\,du - \pi_{00}(v_0 - u_{\pi_0}).$$

"(3) Change the pressure of the vapour to π_π, so that it may be in equilibrium with the solution when under the hydrostatic pressure of its vapour alone; the work done is—

$$-\int_{\pi_{00}}^{\pi} p\,dv.$$

"(4) Close the semi-permeable membrane which separates the solution from the solvent by a shutter to which hydrostatic pressure p_0 can be applied; also enclose the solution by a second shutter, to which a pressure p may be applied [these two steps do not involve work]; the solution may now be removed. Change its pressure to π_π, bring it into contact with the separated vapour of the solvent, which is also at a

[1] In fact, the values of the "natural" vapour pressures go in the opposite direction, *i.e.* the vapour pressure π_π of the solution is *less* than the vapour pressure of the solvent π_{00}, whilst p is, as a matter of fact, *greater* than p_0.

pressure π_π; condense this vapour into it, thereby increasing the volume of the solution by s_π, and then compress to a pressure p. The work done is—

$$-\int_{p}^{\pi_\pi} p dV + \pi_\pi(v_\pi - s_\pi) + \int_{p}^{\pi_\pi} p d(V + s).$$

"The connection through the semi-permeable membrane must now be restored, and then everything will be in its initial state, and the total work done, since the cycle is isothermal, must be zero.

"Adding the several terms, integrating by parts, and simplifying this equation, we obtain—

$$(P_p + p_0)s_p + ps_p - \int_{\pi_{00}}^{p_0} u dp - \int_{p}^{\pi_{00}} v dp + \int_{\pi_\pi}^{p} s dp = 0;$$

or, remembering that $P_p = p - p_0$, [since equilibrium is maintained, as in Fig. 28, by the help of p_0 and p]—

$$\int_{\pi_\pi}^{p} s dp = \int_{\pi_\pi}^{\pi_{00}} v dp + \int_{\pi_{00}}^{p - P_p} u dp \quad . \quad . \quad . \quad (1)$$

"This is the expression which gives the osmotic pressure for any concentration and temperature in terms of the vapour pressures, etc., corresponding to the same concentration and temperature. It includes the influence of compressibility, and states with precision the particular circumstances to which the various physical data correspond. For example, the vapour pressures π_{00} and π_π are the vapour pressures of the solvent and solution *each under the hydrostatic pressure of its own vapour*, and not under the hydrostatic pressures p_0 and p respectively, as might perhaps have been expected.

"In order to compare this equation with those hitherto given, we will first assume that s and u are constants (that is, we ignore compressibility), and that the vapour follows the gas laws. The equation then becomes—

$$(p - \pi_\pi)s + (\pi_{00} - p_0)u = RT \log\left(\frac{\pi_{00}}{\pi_\pi}\right) \quad . \quad . \quad (2)$$

where R is the gas constant for solvent vapour. This may also be written—

$$(P_p + p_0 - \pi_\pi)s + (P_p + \pi_{00} - p)u = RT \log\left(\frac{\pi_{00}}{\pi_\pi}\right) \quad . \quad (3)$$

"The following special cases are of interest.

"1st. Let P_{π_0} be the osmotic pressure when the *solvent* is under the hydrostatic pressure π_{00} of its own vapour. Then $P_{\pi_0} = p - \pi_{00}$, so that $(P_{\pi_0} + \pi_{00} - p)u = 0$; and

$$(P_{\pi_0} + \pi_{00} - \pi_\pi)s = RT \log\left(\frac{\pi_{00}}{\pi_\pi}\right) \quad . \quad . \quad . \quad (4)$$

"This is identical with van 't Hoff's case, except that he writes it in

terms of molecular quantities and pays no attention to the variation of P and π with hydrostatic pressure.

"2nd. Let P_π be the osmotic pressure when the *solution* is under the hydrostatic pressure π_π of its own vapour. Then $P_\pi = \pi_\pi - p_0$, so that $(P_\pi - \pi_\pi + p_0)s = 0$; and

$$(P_\pi + \pi_{00} - \pi_\pi)u = RT \log \left(\frac{\pi_{00}}{\pi_\pi}\right) \quad . \quad . \quad . \quad (5)$$

"This is identical with the Earl of Berkeley's solution, in which, however, no attention was paid to the influence of pressure. It is precisely the result naturally given by the method he employs when attention is paid to pressure.

"*Influence of Hydrostatic Pressure of Solution upon Osmotic Pressure.*

"By differentiating formula (2) with respect to p, the concentration (c) and, therefore, the value of π_π being maintained constant, we get—

$$\left(\frac{dp_0}{dp}\right)_c = \frac{s}{u}, \quad \text{or} \quad \left(\frac{dP}{dp}\right)_c = \frac{u - s}{u}.$$

"This does not allow for compression.

"By differentiating the accurate expression equation (1), we get—

$$\left(\frac{dP_p}{dp_0}\right)_c = \frac{u_{p_0} - s_p}{u_p} \quad . \quad . \quad . \quad . \quad (6)$$

which is of the same form as before, but the terms have now more precise meanings. Similarly, the rate of change of osmotic pressure with change in the hydrostatic pressure of the solvent is given by—

$$\left(\frac{dP_p}{dp_0}\right)_c = \frac{u_{p_0} - s_p}{s_p}. \quad . \quad . \quad . \quad . \quad (7)$$

"*Comparison of Osmotic Pressures of Solutions of different Substances in the same Solvent.*

[Comparing two solutions, different solutes, same solvent.] It is easy to show that the two-fold isotony (for vapour and for osmotic pressures) holds for any hydrostatic pressures of the solutions (the same for all), provided that the vapour pressures be measured for the solutions when *under the same hydrostatic pressure.* This can be shown at once by considering the arrangement represented in Fig. 29.

"Two solutions having the same solvent are contained in a vessel and separated one from the other by a semi-permeable membrane. The space above contains the vapour together with an inert gas whose pressure is A. The vessel is supposed to be in a region free from gravitational action. Then it is obvious that if the osmotic pressures be equal, but the vapour pressures be different, a circulation must ensue which will upset the initial osmotic equilibrium in such a direction as

to maintain the difference of vapour pressures and thus to cause perpetual flow; the possibility of this we are entitled to deny.

"In order to show how this result is consistent with equation (1), it is necessary to find the mode in which the vapour pressures vary with hydrostatic pressure.

"*Variation of Vapour Pressure with Hydrostatic Pressure.*

"An approximate formula for this variation has been obtained by Professor J. J. Thomson in his *Applications of Dynamics to Physics and Chemistry*, by means of the Hamiltonian method.

"The theorem that the vapour pressure of the pure solvent increases with the hydrostatic pressure can be obtained in a very simple way as follows:—

"Let a vertical tube (Fig. 30) containing the solvent be enclosed in

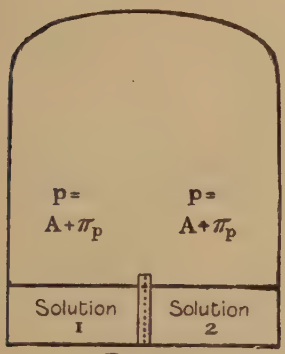


FIG. 29.

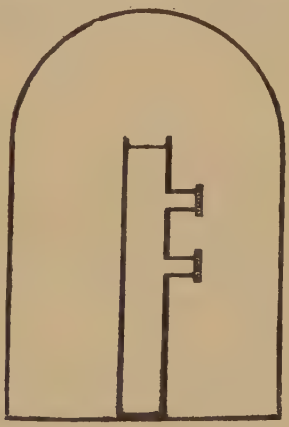


FIG. 30.

a closed chamber *in a gravitational field*, and let equilibrium be set up. Let now membranes permeable to the vapour alone be inserted in the side of the tube at a distance apart dh. Let p_0 be the hydrostatic pressure in the liquid at any point, and $\pi_{0_{p_0}}$ that in the vapour. Then u_{p_0} being the specific volume of the liquid, and $v_{\pi_{0p_0}}$ that of the vapour at the corresponding pressures, we have—

$$dp_0 = -g\frac{dh}{u_{p_0}}, \qquad d\pi_{0_{p_0}} = -g\frac{dh}{v_{\pi_{0_{p_0}}}}$$

whence

$$\frac{\partial \pi_{0_{p_0}}}{\partial p_0} = \frac{u_{p_0}}{v_{\pi_{0_{p_0}}}}.$$

"This method is not applicable to the case of the vapour of a solution, because the concentration of the solution changes with the height.

"We will proceed to find an exact formula for this variation by means of an isothermal thermodynamic cycle, consisting of several stages:—

"A large volume V of solution is taken with a space above containing an inert gas (say, air) and vapour enclosed by a piston semi-permeable to the vapour alone, which is again enclosed by a non-permeable piston (Fig. 31). The semi-permeable piston will experience the pressure A due to the inert gas; the pressure on the non-permeable piston will be the pressure of the vapour alone, which is π_p. The volume of the gas and vapour is initially V_A.

"(1) Evaporate 1 gram of solvent from the solution by withdrawing the outer piston, leaving the inner one fixed; work done upon the system in this process is equal to—

$$As_p - \pi_p(v_{\pi_p} - s_p) \quad \text{or} \quad -\pi_p v_{\pi_p} + ps_p.$$

where v_{π_p} is the specific volume of the vapour at the pressure π_p, and $p = A + \pi_p$.

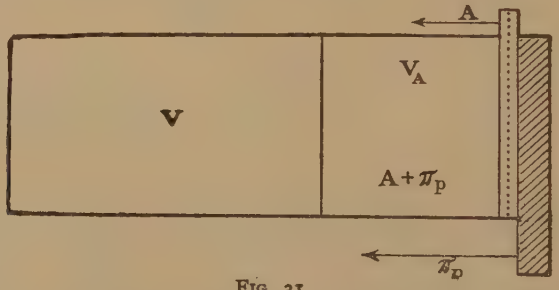


FIG. 31.

"(2) Increase the total pressure to $p' = A' + \pi_{p'}$ by moving both pistons such amounts that no further liquid condenses or evaporates. The work done by the inner piston is—

$$-\int_{p-\pi_p}^{p'-\pi_{p'}} A d(V - s + V_A)$$

and that done by the outer piston is—

$$-\int_{\pi_p}^{\pi_{p'}} \pi d(v + V - s + V_A + V_B),$$

where V_B is a volume which represents the fact that the vapour which at the first pressure was to the left of the inner piston may have passed through it on the change of pressure taking place, since the law of compressibility of the vapour will not in general be the same as for the inert gas A.

"(3) Condense 1 gram of the vapour by moving outer piston from right to left, keeping inner piston fixed.

Work done is— $\pi_{p'} v_{\pi_{p'}} - p' s_{p'}$.

"(4) Restore the original state of the system by suitably moving the two pistons; work done upon the system is—

$$\int_{p-\pi_p}^{p'-\pi_{p'}} \mathrm{A}d(\mathrm{V}+\mathrm{V_A}) + \int_{\pi_p}^{\pi_{p'}} \pi d(\mathrm{V}+\mathrm{V_A}+\mathrm{V_B})$$

where $\int \pi d\mathrm{V_B}$ must be the same as before.

"Since the above represents a complete isothermal cycle the total work is zero; that is, after integrating by parts,

$$\int_p^{p'} s dp = \int_{\pi_p}^{\pi_{p'}} v dp$$

whence—

$$\frac{\partial \pi_p}{\partial p} = \frac{s_p}{v_{\pi_p}} \quad . \quad . \quad . \quad . \quad (10)$$

"It is convenient to take as the upper limits of the two integrals—

$$p' = \pi_\pi \text{ and } \pi_{p'} = \pi_\pi.$$

"This result is for a solution of any concentration; hence, for the pure solvent we have—

$$\int_{p_0}^{p_0'} u dp = \int_{\pi_{0p_0}}^{\pi_{0p_0'}} v dp \quad \text{and} \quad \frac{\partial \pi_{0p_0}}{\partial p_0} = \frac{u_{p_0}}{v_{\pi_{0p_0}}} \quad . \quad . \quad (11)$$

"This last result is identical with the result obtained by Professor J. J. Thomson as an approximate solution; we now see that it is accurate, provided that precise meanings be given to the variables concerned.

"It is convenient to take as the upper limits of these integrals $p_0' = \pi_{00}$ and $\pi_{0p_0'} = \pi_{00}$.

"By means of these equations we can now transform equation (1)—We have—

$$\int_p^{\pi_\pi} s dp = \int_{\pi_p}^{\pi_\pi} v dp.$$

Inserting this in (1),

$$\int_{\pi_{00}}^{p-p+\pi_p} u dp = \int_{\pi_\pi}^{\pi_p} v dp + \int_{\pi_{00}}^{\pi_\pi} v dp = \int_{\pi_{00}}^{\pi_p} v dp \quad . \quad . \quad (12)$$

"These integrals depend only upon the properties of the *pure solvent* and upon the limits of integration.

"The approximate form of the above equation is—

$$(\mathrm{P}_p - p + \pi_{00})u = \mathrm{RT} \log \left(\frac{\pi_{00}}{\pi_p}\right).$$

"When p is the value for which the hydrostatic pressure of the solvent is π_{00}, the left-hand side of this is zero; consequently, in this case $\pi_{00} = \pi_p$ (from the right-hand side). This is simply a special case of a general relation to be proved next.

"Again, inserting the value for both $\int_{\pi_\pi}^{p} sdp$ and $\int_{\pi_{00}}^{p_0} udp$ into equation (1)—

$$\int_{\pi_\pi}^{\pi_p} vdp = \int_{\pi_\pi}^{\pi_{00}} vdp + \int_{\pi_{00}}^{\pi_{0p_0}} vdp \quad \text{or} \quad \int_{\pi_{0p_0}}^{\pi_p} vdp = 0,$$

whence $\pi_\pi = \pi_{0p_0}$.

That is, when a solution is in osmotic equilibrium with the pure solvent, as in Fig. 28, the vapour pressure of the solution *is equal to* the vapour pressure of the pure solvent, *each measured for the actual hydrostatic pressure of the fluid to which it refers.*[1]

"That this is so is almost immediately evident from the following case :—

"The solution and solvent are placed in a vessel and separated by a semi-permeable membrane (Fig. 32). The space above is also separated into two parts by a partition semi-permeable to the vapour of the solvent, but not to an inert gas. A pressure difference $p - p_0 = P_p$ is maintained between the two sides by aid of an inert gas. Then, unless the vapour pressures π_p and π_{0p_0} are equal, a flow of vapour will occur with such consequent evaporation and condensation on the two fluids respectively as to upset the initial osmotic equilibrium in a direction which will maintain the difference of vapour pressures and thus cause perpetual flow, the possibility of which we are entitled to deny. This conclusion may be taken as a check upon the equations which we have derived.

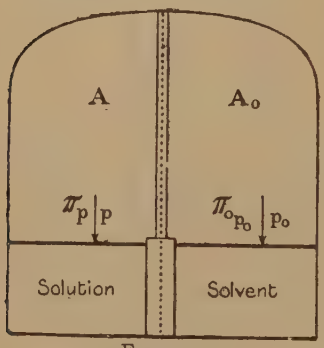


FIG. 32.

"We have considered only the case of a non-volatile solute, but it is easy to see that this theorem must be equally true if the solute is volatile; for the upper partition may be taken impermeable to the vapour of the solute; and the argument is, in such a case, in no way changed.

"*Standard Conditions of Measurement.*

"In whatever experimental ways osmotic pressures may be determined, it is necessary to decide on the standard conditions to which the obtained values shall be reduced for the purposes of tabulation and

[1] *I.e.* the solution is under a hydrostatic pressure p, the solvent is under a hydrostatic pressure p_0, such hydrostatic pressure being produced by an inert gas.
This conclusion is one of the most important points of Porter's theory of osmotic pressure.

comparison; that is, to what hydrostatic pressure shall they refer? When osmotic pressures are compared by De Vries' original method, as they still often are (by means of vegetable or animal cells), the *solution* is under only a moderate pressure. On the other hand, when values are obtained by the method adopted by the Earl of Berkeley, it is the *pure solvent* that is under a moderate pressure. The values of the osmotic pressure will differ in general in the two cases.

"Now it seems most natural to reduce always either to the value corresponding to the solvent under its own vapour alone or to that corresponding to the solution under its own vapour alone; and of these two, the latter seems the better. It is indeed most natural of all to think of the osmotic pressure as being a property of the solution (just as its

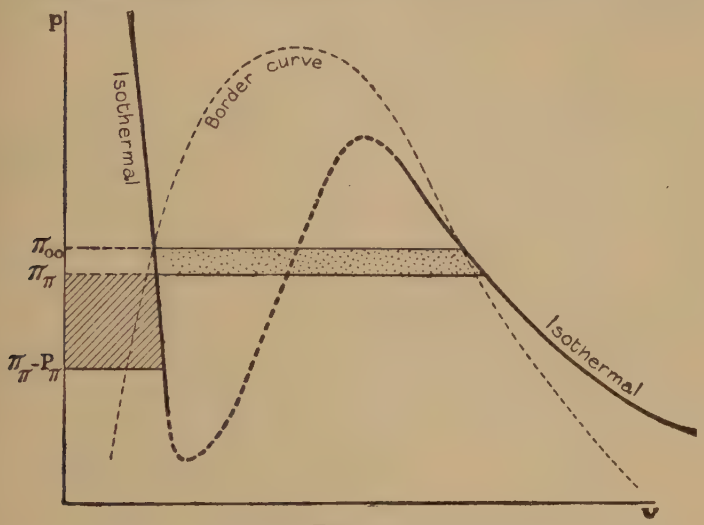


FIG. 33.

vapour pressure, volume, etc., are), the pure solvent being only brought into consideration in a secondary way in connection with an experimental mode of determining the osmotic pressure. It may be objected that if this standard be adopted the equilibrium pressure of the pure solvent will, even for moderate strengths of solution, usually be negative; that is, the solvent would require to be under tension. The difficulty is relieved when it is remembered that a certain amount of tension in liquids is practically possible, and the osmotic pressure for a strong solution might always be conceived as being measured against a less strong solution, and this in turn against a less, and so on, till the pure solvent was reached. If this standard be adopted, we have, from equation (1)—

$$\int_{\pi_{\pi}-P_{\pi}}^{\pi_{00}} u dp = \int_{\pi\pi}^{\pi_{00}} v dp$$

an equation which is capable of being graphically represented on the indicator diagram for the pure solvent (Fig. 33).

"The equation, in fact, states that the hatched area must be taken equal to the dotted area; the vertical height of the former then gives the osmotic pressure."

Porter's equation has been applied by O. Wood to the calculation of the osmotic pressure from the results of vapour pressure measurements obtained in connection with concentrated solutions of sucrose in water at a series of different temperatures (*cf.* Wood, *Trans. Faraday Soc.*, 1915). Porter (*Trans. Faraday Soc.*, 1915) has further considered von Babo's law, and Kirchhoff's equation for the latent heat of dilution of a solution, laying special emphasis on the assumptions introduced into the deduction of the expressions as obtained in their usual form. The reader is referred to the paper for details.

Liquid Mixtures.

These are solutions in which the vapour pressure of the solute cannot be regarded as negligible compared to that of the solvent—in fact the terms solute and solvent are not very applicable, as both liquids may be present in large amount. Such systems have been examined theoretically and practically by Dolezalek (*Zeitsch. physik. Chem.*, **64**, 727, 1908; *ibid.*, **71**, 198, 1910); see also Stern, *loc. cit.*, and Washburn (*Journ. Amer. Chem. Soc.*, **32**, 670, 1910). The following simple relation has been put forward by Dolezalek as being of fundamental importance in these cases. The partial vapour pressure p_a of a component a present in the liquid state is proportional to the molecular concentration of the component a in the liquid state when such concentration is expressed as a fraction of the total number of moles present. If x_a is the fractional molar concentration of a in the liquid state at a given temperature, and p_0 is the vapour pressure which the liquid a *alone* would exert, then the partial pressure of a in the mixed vapour is given by p_a where—

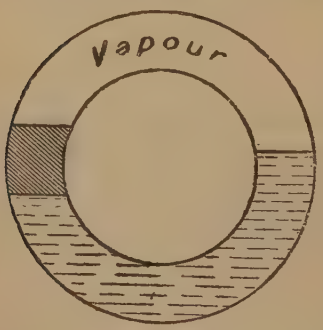


Fig. 34.

$$p_a = p_0 x.$$

Washburn (*loc. cit.* and *Trans. Amer. Electrochem. Soc.*, **22**, 330, 1912) has shown in the following manner that this simple relation can only hold if the liquids composing the system are perfectly miscible. Thus, suppose we had a system consisting of two liquid layers in a tube (Fig. 34) in equilibrium, the component a being present in each layer. On the above assumption we will have for the vapour pressure of a above the one layer the expression—

$$p_{a_1} = p_0 x_1$$

and similarly for the other the vapour pressure of *a* is—

$$p_{a_{II}} = p_0 x_{II}$$

But since perpetual motion (distillation of *a viâ* the vapour, from one layer to the other) is impossible, it is necessary (by the Second Law of Thermodynamics) that $p_{a_I} = p_{a_{II}}$ and hence $x_{a_I} = x_{a_{II}}$. That is, the molar concentration of *a* in both layers is identical. But this is applicable to all the molecular species present in each layer, and hence both layers are identical, and cannot therefore form two phases. We must therefore conclude that the above simple vapour pressure law only holds for mixtures composed of *perfectly* miscible liquids and cannot apply to the cases in which partial miscibility exists. The problem of liquid mixtures is in a rather rudimentary stage at present, and further discussion of it in a book of this kind must be omitted.[1]

[1] In addition to the references given, the reader should consult the papers of Rosanoff and Easley (*Journ. Amer. Chem. Soc.*, 31, 953, 1909; *Zeitsch. physik. Chem.*, 68, 641, 1910), and especially the chapter devoted to the subject in Partington's *Thermodynamics*.

CHAPTER X.

Equilibrium in heterogeneous systems, in the absence of electrical, capillary, or gravitational effects—The Phase Rule and some of its applications—The theory of Allotropy.

In Vol. I. the question of heterogeneous equilibrium, *i.e.* equilibrium in a system consisting of more than one phase, was considered from the kinetic standpoint, the generalisation employed being the Distribution Law of Nernst. We now take up the study of heterogeneous equilibrium from the standpoint of thermodynamics.

Thermodynamical Deduction of the Nernst Distribution Law.

We can deduce the Distribution Law by means of a simple thermodynamic cycle carried out at constant temperature.

Thus, consider the two equilibrium systems I. and II. (Fig. 35),

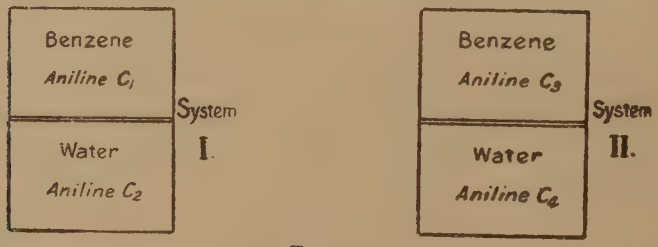


Fig. 35.

each consisting of two phases in contact (say, water and benzene) with a solute (say, aniline) distributed between each pair of phases. Suppose in system I. the concentration of the aniline in the water and benzene is c_1 and c_2 respectively. In system II. the concentrations are c_3 and c_4 respectively. The systems are both at the same temperature. Suppose the molecular state of the aniline is the same in the water as it is in the benzene, and further suppose that the solutions are all sufficiently dilute to allow of the application of the gas law. It is required to show that—

$$\frac{c_1}{c_2} = \frac{c_3}{c_4} = \text{constant.}$$

1st Step.—Suppose a small quantity δn gram-moles of aniline are removed from the benzene solution in I. and transferred to the benzene

solution in II. isothermally and reversibly. The maximum work done at constant temperature (and practically constant volume) is—

$$\delta n \mathrm{RT} \log \frac{c_1}{c_3}.$$

2nd Step.—Now suppose the quantity δn at c_3 passes at constant temperature and volume into the water layer at concentration c_4. No work is done, since the system (II.) is in equilibrium.

3rd Step.—Transfer the quantity δn from the water layer in II. to the water layer in I. The maximum work done is—

$$\delta n \mathrm{RT} \log \frac{c_4}{c_2}.$$

4th Step.—Allow the quantity δn to pass into the benzene layer in I. Since the system I. is in equilibrium, this transfer at constant temperature and volume involves no work. The cycle is now completed, and since it has been carried out isothermally and reversibly it follows from the Second Law that the total work is zero. That is—

$$\delta n \mathrm{RT} \log \frac{c_1}{c_3} + \delta n \mathrm{RT} \log \frac{c_4}{c_2} = 0,$$

or

$$\frac{c_1}{c_3} = \frac{c_2}{c_4} \text{ or } \frac{c_1}{c_2} = \frac{c}{c_4} = \text{constant}$$

which was to be proved.

Having already given considerable experimental illustrations of the principal of the Distribution Law, it is unnecessary to consider it further here. Instead we shall take up the subject of heterogeneous equilibrium from a much more general standpoint.

The Phase Rule.

Following this method we arrive at an important generalisation called the Phase Law, or Phase Rule, first deduced by Willard Gibbs in 1878 (*cf.* Gibbs' *Scientific Papers*, published by Messrs. Longmans) by means of his "chemical potential" method. Gibbs' Rule received, however, no practical application until it was taken up by the Dutch physical chemist, Bakhuis Roozeboom, who showed in a series of classical researches, the fundamental importance of the principle as a guide to the behaviour of heterogeneous chemical systems (*cf.* B. Roozeboom's book, *Heterogene Gleichgewichte*, which has recently been re-edited and extended by Meyerhoffer). The original method of deducing the Phase Rule employed by Gibbs is by no means simple, and many alternative methods have since been described by various authors. A good method is given in Nernst's *Theoretical Chemistry*. In the following pages an attempt is made to deduce the principle, first of all by a very simple method based on that suggested by J. A. Muller (*Comptes Rendus*, **146**, 866, 1908), and secondly a more rigid thermodynamical method is given for those who have followed the chapter on more

advanced thermodynamic principles in Chap. II. of this book. It must be emphasised that the Phase Rule *per se*, while extraordinarily useful, could not hold its important position were it not that at the same time we make use of the Le Chatelier-Braun principle of "mobile equilibrium". The importance of the simultaneous application of both principles has been emphasised by W. D. Bancroft, in the introduction to his book, *The Phase Rule*. Within the confines of a single chapter it is obviously impossible to give more than the briefest outline of the applicability of the Phase Rule to a very few typical examples. In order to grasp the full significance of the Phase Rule, the reader is therefore recommended, after reading this chapter, to consult the work of Findlay on *The Phase Rule* and Desch's *Metallography*, in this series of textbooks, and, above all, Roozeboom's book already referred to.

Before proceeding to consider the Phase Rule itself, it is necessary to obtain a clear idea of what is meant by the terms *phase*, *component*, and *degrees of freedom*. Findlay (*loc. cit.*) defines them thus: "A heterogeneous system is made up of different portions, each in itself homogeneous but marked off in space, and separated from the other portions by boundary surfaces. These homogeneous, physically distinct and mechanically separable portions are called *phases*." Thus ice, liquid water, and vapour (steam) are three phases of the same chemical substance, water. A system may be made up of any number of coexisting phases. It is important to remember, however, that in any system there can never be more than *one* vapour phase, because all vapours and gases are miscible in all proportions. Thus take the classic case of heterogeneous equilibrium, namely, the dissociation of calcium carbonate. The system here considered is made up of two solid phases, *i.e.* calcium carbonate and lime, one gas or vapour phase which is practically entirely carbon dioxide, though we must imagine that there are a few molecules of lime and calcium carbonate present, since all substances have a vapour pressure, even though it is extremely small in the case of most solids. This system consists therefore of three phases. Again, consider the case of ammonium chloride partly in the solid and partly in the gaseous state. There is one solid phase, namely, solid ammonium chloride. There is one vapour state consisting of ammonia gas and hydrochloric acid gas, and a small quantity of undissociated ammonium chloride vapour. This heterogeneous system consists of two phases. The system containing a solid substance in contact with a saturated solution of that substance, and vapour above the liquid, consists of three phases, one solid, one liquid (the solution), and one vapour. It is important to bear in mind *that in phase equilibrium the equilibrium is independent of the absolute mass or amount of the phases.* Thus in the case of calcium carbonate in equilibrium with lime and carbon dioxide, the position of equilibrium (determined, say, by the vapour pressure value as we saw from the standpoint of the Law of Mass Action) is quite unaltered by further addition of calcium carbonate or lime. The vapour pressure of a liquid is unaltered by increasing or diminishing the quantity of the liquid. Also the concentration (saturated) of solid

dissolved by a given liquid is independent of the quantity of solid in contact with the liquid. If in the $CaCO_3 - CaO - CO_2$ system we had simply increased the volume of the gas phase by expanding the containing vessel, some more of the $CaCO_3$ would dissociate, the pressure would again take on its original value although the absolute amount of the vapour phase is greater than in the first state. Similarly if we diminish the absolute amount of the vapour phase in the above case by diminishing the volume of the vessel, we leave the equilibrium point unchanged. Also if CO_2 gas were added to the system, the pressure would remain constant, *i.e.* the equilibrium would be unaltered, as long as any CaO remained unchanged into carbonate (since the formation of solid $CaCO_3$ is the process which occurs in order to keep the CO_2 pressure constant). When enough CO_2 had been added to change *all* the CaO into $CaCO_3$, the gas pressure would begin to rise (on further addition of CO_2), but this alteration in the equilibrium point is not unexpected, when we consider that we have altered the *nature* of the system by causing one of the phases (CaO) to entirely disappear as such. Under these circumstances the alteration in pressure on adding the CO_2 is exactly what we would predict on the basis of the Phase Rule.

Having made clear what is meant by the term phase, we have to consider the meaning of another term—*component*. A phase is made up of one or more chemical substances or constituents. It might be thought that these constituents also represent the components of the system. This, however, is only partly correct. By the term components is meant those constituents the concentration of which can undergo independent variation in the different phases. Findlay (*loc. cit.*) gives the following definition:—

"*As the* components *of a system there are to be chosen the* smallest number *of independently variable constituents, by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.*"

The idea will be made clearer by considering a few examples.

Take the case of the system liquid water and steam in equilibrium. The number of components is *one*, namely, the chemical constituent H_2O. The system consists of two phases, namely, liquid and vapour, but the one component (H_2O) is all that is necessary to cause the formation of either phase. At the so-called triple point at which we have ice, liquid water and vapour coexisting, again the system is a one-component one, although existing in three phases. The actual chemical constituents, say, in the solid and liquid phases, can be represented by $(H_2O)_3$ and $(H_2O)_2$ or other polymers, but these are all directly produced from the one component H_2O. Take another case, namely, the system consisting of copper sulphate penta-hydrate and trihydrate, in contact equilibrium with water vapour. The solid phases are $CuSO_4 . 5H_2O$ and $CuSO_4 . 3H_2O$. The vapour phase consists practically entirely of H_2O, namely, water vapour. The number of phases is *three*, one vapour and two solid. The number of components (or independent variable constituents) is *two*, namely, $CuSO_4$ and H_2O.

Out of these two components we can build up each phase. Thus the penta-hydrate solid is made up of one molecule of $CuSO_4$ and five molecules of H_2O. The solid trihydrate is made up of one molecule of $CuSO_4$ and three molecules of H_2O. Note that the ratio of the molecules of $CuSO_4$ and H_2O must be taken as independent. It would not do to take them in a fixed ratio, say 1 to 5, for this would allow us to form the penta-hydrate, but not the trihydrate. If we had assumed their ratio constant we would be dealing with one component only, namely ($CuSO_4 . 5H_2O$). This is not sufficient for the present case. The vapour phase can also be chemically represented by the two components named by taking zero number of $CuSO_4$ molecules together with one H_2O. Again, take the similar case of the $CaCO_3$—CaO—CO_2 equilibrium. Here again we have a *two*-component system. The components may be either CaO and CO_2 or $CaCO_3$ and CO_2. Take the first choice, namely, CaO and CO_2, thus the solid $CaCO_3$ phase can be represented by one molecule of CaO + one molecule of CO_2. The CaO solid phase can be represented by one molecule of CaO and zero molecules of CO_2. The vapour phase can be represented by one mole of CO_2 and zero molecules of CaO. (Note that zero as well as positive and negative values are permissible.) In this case also, in order to represent each phase, we must again regard the CaO and CO_2 as *independently* variable, *i.e.* the system consists of two components. Now take the case of solid ammonium chloride, in contact with its vapour which consists of some NH_4Cl and mainly of NH_3 and HCl in equivalent molecular proportions. The number of components in this case is *one*, namely, the chemical entity ammonium chloride. Thus the solid phase is represented by NH_4Cl. The vapour phase is also represented by the formula NH_4Cl, for although we have two gases present, namely, NH_3 and HCl, these are in the stoichiometric ratio represented by the formula NH_4Cl. The undissociated molecules of ammonium chloride present in the vapour are simultaneously represented by NH_4Cl. This is a good illustration of the distinction between chemical constituents and components. In the vapour, for example, we have three chemical constituents, namely, ammonium chloride undissociated gas, ammonia gas, and hydrochloric acid gas, but they are all formed from one component, ammonium chloride. In this case it is unnecessary to assume two independent constituents, *i.e.* components, say NH_3 and HCl, for the composition of both phases can be represented by the two substances NH_3 and HCl in a fixed molecular ratio $\frac{1 \text{ mole } NH_3}{1 \text{ mole } HCl}$. They need not be independently variable. This will illustrate the significance of the term "*smallest number*" of independently variable constituents in the definition of component. A further important point may be illustrated by the ammonium chloride case. Suppose we add NH_3 or HCl gas, so that one or other of these is in excess in the gas phase, then the composition of the gas phase can be no longer represented by the ratio $\frac{1 \text{ mole } NH_3}{1 \text{ mole } HCl}$, *i.e.* by the one component (NH_4Cl), and we have now to

regard the system as containing *two* components, NH_3 and HCl. These being independently variable constituents, we can form all the phases by their means. Under these conditions the ammonium chloride dissociation becomes analogous to the calcium carbonate or copper sulphate-hydrate equilibrium. As regards nomenclature it is usual to denote the number of *phases* of a system by r and the number of components by n. We may conclude this discussion of what is meant by the components of a system, by quoting another definition of component, namely, that given by Kuenen (*Proc. Roy. Soc. Edin.*, **23**, p. 317, 1899—1900):—

"In determining n we must not count separately those substances which in all the phases (either separately or in combination with others in the ratio in which they occur in the same phase) may be formed out of those that have already been counted, with the additional understanding that if we obtain different results for the total number, by counting in a different order, we are to take the smallest of the numbers found."

Having defined the terms *phase* and *component* we have now to consider a further term, namely, *the degrees of freedom*[1] *of a system.*

In deducing the conditions for equilibrium in a heterogeneous system, *i.e.* in deducing the Phase Rule, Gibbs regarded every system as defined by the three independent factors or *variables*—temperature, pressure, and the concentrations of the components in each phase. Now in dealing with equilibrium from the standpoint of thermodynamics, there are certain "thermodynamic criteria of equilibrium," such as those with which we have already become acquainted. These criteria take the form of thermodynamic equations containing terms called thermodynamic potentials characteristic of each component, the equilibrium being reached when these potentials reach certain values. (One such potential of which we have made frequent use is the free energy of a component. This, however, cannot be conveniently employed here.) By means of these equations it is possible to fix the values of a certain number of the variables of the system, in fact as many variables as there are equations. But the number of variables actually possessed by a system may be greater than the number of thermodynamic equations. The difference between the number of variables and the number of equations gives the number of variables which are left undefined by the equations. These variables, which are really variable at will, are called the *degrees of freedom of the system.* Of course, as long as no definite values are assigned to these variables the equilibrium of the system as a whole will remain undetermined. Findlay's definition (*l.c.*) of degrees of freedom of a system is as follows: "The number of degrees of freedom of a system are the number of variable factors, temperature, pressure, and concentration of the components, which must be arbitrarily fixed

[1] The term degrees of freedom in the present case must not be confused with the same term already referred to in dealing with the possible modes of motion of molecules and atoms. *Cf.* the section dealing with specific heat and energy quanta, Vol. III.

in order that the conditions of the system may be perfectly defined". This will be better understood by considering a few examples. Take the case of liquid water in contact with water vapour. This is a two-phase, one-component system. We know as a fact of experience that these two phases can coexist over a considerable range of temperature, without either disappearing or any new phase appearing. If we arbitrarily fix the temperature of the system (say 25° C.), we know also as a fact of experience that the pressure will take up a certain equilibrium value, namely, the pressure of saturated water vapour at 25° C., and the system will remain in this state for infinite time. On altering the temperature to another value (within limits) other equilibrium positions will be taken up. In fact, in this simple case the temperature of equilibrium is entirely defined by one arbitrary variable, the temperature. That is, this system possesses one degree of freedom. We shall see later how this is predicted by the Phase Rule. Suppose, however, that we lower the temperature of the system until ice makes its appearance. The system then consists of three phases—ice, liquid water, vapour. It is a fact of experience that these three phases can only coexist in equilibrium at a single *point*, *i.e.* at a single value of temperature and pressure, the so-called triple point, which is approximately 0° C. In this case we cannot alter any variable at will, for if we alter, say, the temperature by raising it, the system will change in the sense that ice will disappear, and we are no longer dealing with the equilibrium of the *three* phases. Similarly, if we lower the temperature, the liquid will entirely change into ice, and we are left with the two-phase equilibrium, solid—vapour. A system which can only exist at a single point is easily determined by the thermodynamic criteria, or equations which now fix all the variables. The system ice—liquid water—vapour is said to possess no degrees of freedom or to be invariant. If, on the other hand, we consider again the liquid water—vapour case, and raise the temperature beyond the critical point, *i.e.* beyond the point at which the liquid water can exist at all, the system will change entirely into one phase, the vapour, and this vapour can exist as such under changes of both temperature and pressure. That is, the system possesses two degrees of freedom. Note, we look upon the persistent existence of a phase as the *experimental* evidence for believing that the phase represents an equilibrium or stable state. In the above simple case we have not had to consider concentration variables, for the system is one component (concentration being defined as the ratio of one component to another). Hence the concentration in each phase remains constant throughout. Let us now take a case in which concentration changes can occur, namely, the two-component system H_2O—NaCl. Suppose we consider first of all the aqueous solution in contact with vapour. How many independent variables, *i.e.* degrees of freedom, does such a system possess? Let us arbitrarily choose a certain strength of solution, say $\frac{N}{10}$. Let us also select a certain temperature, then the vapour pressure will automatically fix itself and equilibrium will be maintained,

the pressure being that of water vapour (saturated) over the salt solution of concentration $\frac{N}{10}$. (This vapour pressure we already know is less than the vapour pressure over pure water at the same temperature.) Before equilibrium could be fixed it was necessary to assign arbitrary values to the two variables, concentration and temperature. That is, the two-phase system considered possesses *two degrees of freedom.* Of course the actual choice of variables to which we wish to assign arbitrary values would not necessarily be the temperature and concentration, although these are the most convenient in the above illustration. Thus let us suppose that we assign a certain pressure and temperature to the system. Then in order that the system may realise these and at the same time be in equilibrium we must alter the *concentration* of the salt to suit. Hence the concentration of the system is not an arbitrary quantity, but is defined by the fact of having assigned arbitrary values to the temperature and pressure. Again we see that the system has two degrees of freedom (*i.e.* is bivariant) although our choice of the actual arbitrary variables differs from that in the first case. In an exactly analogous way we could have chosen, arbitrarily, a certain *pressure* and *concentration*, and we would have found it necessary to alter the *temperature* of the system in order that the system might reach an equilibrium state corresponding to the arbitrarily chosen pressure and concentration values. Suppose now we cause a new phase to make its appearance, say ice. The system must be cooled down, of course. Suppose we fix the concentration of the solution. Then it will be found that such a solution "freezes at a certain temperature". This is the same thing as saying that the system ice—liquid solution of salt of fixed concentration—vapour can coexist in equilibrium at a single temperature and pressure. Having fixed the concentration of the solution, the equilibrium of the three phases is altogether fixed. That is, the system possesses one degree of freedom (the concentration in this case). If we alter the concentration of the solution, say, by increasing it, the solution will freeze at a lower temperature. That is, once more equilibrium is obtained, but the fact of altering the concentration has caused a concomitant change in the temperature and pressure of the system. We might choose any *one* of the variables, temperature or concentration, but it will be found that having arbitrarily fixed the value of *one* all others are thereby fixed too, *i.e.* we cannot assign arbitrary values to two variables simultaneously. If we attempt to do so the system will alter in respect of the number of its phases, *i.e.* the ice may disappear, for example. Having illustrated what is meant by a "degree of freedom," we can now proceed to the deduction of the Phase Rule—a generalisation which allows us to predict many of the facts already referred to as having been experimentally obtained.

Statement of the Phase Rule.

The Phase Rule states that *a system consisting of n components and r phases is capable of* $(n - r + 2)$ *independent variations.* That is, the

number of independently variable quantities or "degrees of freedom" of such a system is $(n - r + 2)$. This refers, of course, to the equilibrium state finally reached. Denoting the number of degrees of freedom by f, we can write the Phase Rule in the form of the equation—

$$f = n - r + 2.$$

This generalisation holds good for all cases in which electrical, capillary, gravitational, and radiational effects are absent or negligible. Before proceeding to the deduction of the Phase Rule it is necessary to understand what is meant by "*the number of variables of a system*".

In any system one can alter the temperature and pressure. These represent two of the variables of the system, but they do not represent all the variables. It is evident that components can be present at different concentrations, and hence the number of *concentration variables* must also be taken into account. Let us fix our attention on one of the components only, which we may denote by a. Concentration terms are essentially *ratio terms*, say, the ratio of the number of molecules of the given component (a) in a given phase to the *total* number of molecules of all sorts which go to make up the composition of the phase. If there are n components in each phase, the number of such concentration terms is evidently $(n - 1)$ for each phase. Thus suppose a phase to consist of two components, *i.e.* a solution of common salt in water. The composition of the phase is completely determined when we know *one* ratio, *i.e.* one concentration, namely, the ratio of $\frac{\text{molecules of salt}}{\text{molecules of salt and water}}$. For three components, two salts and water, the composition of the solution is defined when we know the ratio of $\frac{\text{molecules of 1st salt}}{\text{total molecules in phase}}$ and $\frac{\text{molecules of 2nd salt}}{\text{total molecules in the phase}}$. That is, one ratio or concentration term is sufficient to define the composition of a phase consisting of two components, two ratios or concentration terms are sufficient to define the composition of a phase containing three components, and therefore $(n - 1)$ ratios or concentration terms are sufficient to define the composition of a phase containing n components. If the system as a whole consists of r phases (there being in each phase n components) evidently the total number of concentration ratios or concentration variables is $r(n - 1)$. Hence *the total number of variables* possessed by a system consisting of n components in r phases is—

$$r(n - 1) + 2.$$

Deduction of the Phase Rule by means of the Thermodynamic Potential Φ.[1]

In the chapter (this Vol., Chap. II.) on the more advanced treatment of thermodynamics, it has been pointed out that the value of the

[1] Compare Duhem, *Journ. Physical Chem.*, **2**, 34, 1898.

quantity Φ, the thermodynamic potential of a substance, can be employed as a criterion of equilibrium, equilibrium being reached when Φ is a minimum. The Φ of a single substance varies with the temperature and pressure. As long as we keep to pure substances (*i.e.* one-component systems), such as liquid water in contact with vapour or ice, the equilibrium is determined by temperature and pressure alone, since concentration is necessarily constant, being always unity. If the temperature and pressure of the liquid phase is equal to the temperature and pressure of the gaseous or solid phase, then we know that the Φ of each phase is the same. When concentration terms enter, however, the Φ of a component depends on its concentration in a phase as well as on the temperature and pressure of the system. If we consider a substance, *i.e.* a component distributed between two phases, both phases being at the same temperature and pressure, we can say that equilibrium distribution will be obtained when the Φ of the component in the first phase = the Φ of the same component in the second phase. Throughout a system consisting of many phases (say r phases), each component being present to a greater or smaller extent in every phase, equilibrium with respect to any one of the n components is reached when the Φ of that component has the same value in every phase. Consider such a system consisting of n components in r phases, and let us fix our attention on one component which we can denote by a. Suppose an infinitely small quantity dm_a of component a is transferred from the first phase to the second phase. The *decrease* in the Φ of the component a in the first phase, which we can denote by Φ_{a1} is given by the expression—

$$-\frac{\partial \Phi_{a_I}}{\partial m_a}.$$

The *increase* in the Φ of the same component in the second phase is given by—

$$+\frac{\partial \Phi_{a_{II}}}{\partial m_a}.$$

Now if the system is in equilibrium as a whole the component a must have distributed itself in equilibrium throughout all the phases, and therefore between the first and second phases. But the criterion of the equilibrium distribution of the component a (the temperature and pressure of which we have kept constant, having simply made a *virtual* variation in the concentration) is that Φ_a shall have remained unchanged; that is $\partial \Phi_a = 0$. But—

$$\partial \Phi_a = -\frac{\partial \Phi_{a_I}}{\partial m_a} + \frac{\partial \Phi_{a_{II}}}{\partial m_a} = 0,$$

or

$$\frac{\partial \Phi_{a_I}}{\partial m_a} = \frac{\partial \Phi_{a_{II}}}{\partial m_a}.$$

Note these are partial differentials, temperature and pressure being

assumed constant. Similarly considering the equilibrium distribution of the same component a between the second and third phases, we would obtain another equation for the equilibrium, *viz.*—

$$\frac{\partial \Phi_{a_{II}}}{\partial m_a} = \frac{\partial \Phi_{a_{III}}}{\partial m_a}.$$

Thus the equilibrium of *one* component distributed between three phases (I., II., and III.) is defined by two equations. Hence the number of equations dealing with the distribution of *one* component amongst r phases would be $(r - 1)$. If we now consider each component in turn, distributed throughout the r phases, the total number of thermodynamic equations would be $n(r - 1)$.

The number of variables possessed by a system containing n components in r phases has been shown in the preceding section to be—

$$r(n - 1) + 2.$$

Hence the number of degrees of freedom f which represent the number of variables for which there are no equations is evidently the difference between the total variables and the total equations, *viz.*—

$$r(n - 1) + 2 - n(r - 1)$$

or

$$f = n - r + 2.$$

Note on the Preceding Deduction of the Phase Rule.

Attempts have been made from time to time to "deduce" the Rule by employing somewhat simpler conceptions than that of the thermodynamic potential. The following, for example, has been suggested by J. A. Muller (*Comptes Rendus*, **146**, p. 866, 1908). Equilibrium of a component throughout a system (of n components in r phases) is obtained when the mass m of the component passing per second from Phase I. to Phase II. is equal to the mass m' of the same component passing per second from Phase II. to Phase I. That is, as a kinetic criterion of equilibrium we have $m = m'$. Considering the same component throughout all the phases we obtain $(r - 1)$ similar equations, and hence for n components we obtain $n(r - 1)$ equations. The total number of variables being $r(n - 1) + 2$, and the number of degrees of freedom f—

$$f = r(n - 1) + 2 - n(r - 1) = n - r + 2$$

which is the Phase Rule. It will be evident, however, that such a method of procedure is open to serious doubt. Prof. W. B. Morton[1] suggests the following criticism:—"In the proof of the Phase Rule the essential thing is that when two phases are in equilibrium, in contact, then the condition of equilibrium is expressed by the equality of *some function* of the variables for one phase, to *some function* of those same variables for the other phase. That this function is Φ is immaterial to

[1] Private communication.

the proof, which is concerned only with the number of the equations and not with their particular form. Of course one admits that equilibrium can be expressed by *some* equation connecting the variables of the two phases concerned. But this is not enough—for there might then be as many equations as there are *pairs* of phases. The equations might be written thus:—

$$F(I, II) = o, F(I, III) = o, F(II, III) = o$$

and so on, where F stands for some function connecting the phases. The number of equations of this type reckoned for r phases is obviously $\frac{1}{2}r(r - 1)$ in all (instead of the number $(r - 1)$ which appears in the Phase Rule deduction). It is essential that $F(I, II) = o$ should be expressible in the form $\Phi_I = \Phi_{II}$, *i.e.* that it should be possible to *separate* the variables of one phase from those of the other, and that the collection of variables in Phase I. indicated by Φ_I should be independent of the other phase coupled with it in the equation. Then and only then, do the equations reduce to the set—

$$\Phi = \Phi_{II} = \Phi_{III}, \text{ etc., or } (r - 1) \text{ in number."}$$

The kinetic deduction referred to above appears to make the assumption that the mass of a component leaving a phase per second is *independent* of the other phase into which it passes, *e.g.* that Phase II. loses per second as much of each component into Phase I. as into Phase III. This is by no means obvious. We have only to think of common salt diffusing on the one side into an acetone phase in which its solubility is extremely small, and on the other into an aqueous phase, to see that the quantities passing out into the two phases per second will in all probability be very different. Granting, however, that the same mass per second does travel from II. to III. as from II. to I., then m is the mass of the component leaving Phase I. per second, and this may be regarded as a function of the variables in Phase I. only, and corresponds therefore to the "some function" mentioned above. The deduction proceeds then, m taking the place of Φ (m might be regarded perhaps as a sort of kinetic measure of Φ). It will be clear, however, that the kinetic method of the kind employed by Muller is open to much doubt.

Classification of (Heterogeneous) Systems by Means of the Phase Rule.

The most convenient method of grouping is according to the number of components forming the system.

One-Component Systems.

Typical instances are—

Component.	Possible Phases.
Water	Solid—liquid—vapour.
Sulphur	,, ,, ,,
Tin	,, ,, ,,

Two-Component Systems.

Components.	Possible Phases.
CaO, CO_2	Solids: ($CaCO_3$, CaO)—gas (CO_2).
$CuSO_4$, H_2O . . .	Solids: $CuSO_4 \cdot 5H_2O$, $CuSO_4 3H_2O$, $CuSO_4$, ice—liquid: solutions—water-vapour.
$FeCl_3$, H_2O . . .	Solids: $FeCl_3$ anhydrous and several hydrates, ice—liquid: solutions—water-vapour.
Na_2SO_4, H_2O . . .	Solids: anhydrous salt, hepta and deka hydrate, ice—liquid: solutions—water-vapour.
Fe, C	Solids: alloys (steels)—liquid—vapour.

Three-Component Systems.

Components.	Possible Phases.
Two salts *with* a common ion—H_2O . . . NaCl—KCl—H_2O . . KCl—$MgCl_2$—H_2O . . NaO—$(CH_3CO)_2O$—H_2O[1].	Several solids—solution—vapour.

Four-Component Systems.

Components: Two salts *without* a common ion (so-called reciprocal salt pairs such as sodium chloride and ammonium bicarbonate) and water in addition. This particular system is that occurring in the ammonia soda or Solvay process of formation of sodium carbonate.

Possible Phases: several solids—solution—vapour

One-Component Systems: Component H_2O.

We shall consider the conditions of equilibrium in some of the systems to which this component can give rise. Take the system—

Liquid water—water vapour in contact.

This system consists of two phases. Applying the Phase Rule, since $n = 1$ and $r = 2$, we get—

$$f = n - r + 2 = 1 - 2 + 2 = 1.$$

This system possesses one degree of freedom, *i.e.* a univariant system. That is, if we arbitrarily fix the temperature, say, then the system as a whole will assume a certain equilibrium state. By choosing a series of temperature values we obtain a corresponding series of equilibrium states. This can be indicated on a temperature pressure diagram by means of the usual vapour pressure curve (*cf.* Fig. 36). On a diagram

[1] Dunningham, *Trans. Chem. Soc.*, 101, 431, 1912.

such as this an invariant system (*i.e.* a system without any degrees of freedom) is represented by a point. A univariant system is represented by a line, *e.g.* the liquid water—vapour curve OA. Bivariant systems,

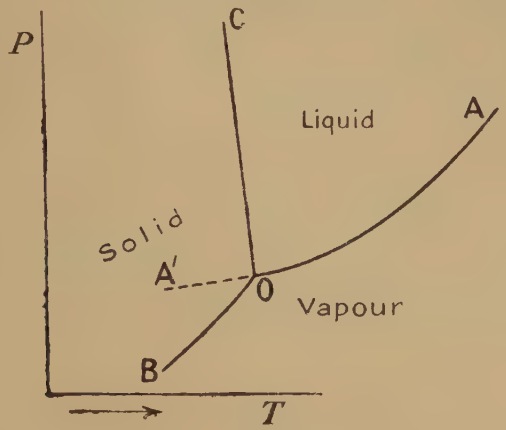


FIG. 36.

or systems having two degrees of freedom are represented by areas. The upper limit A is the critical point, *viz.* 364·3°, and 194·6 atmospheres pressure.

System: Solid water (ice)—vapour.

This being also a univariant system must be represented by a line, *viz.* OB. This has the same significance for the solid—vapour system as the vapour pressure curve had for the liquid—vapour case. In fact, OB is a vapour pressure curve, or, as it is more usually called when solid gives rise to vapour, a sublimation curve. Since ice melts at 0° C. under atmospheric pressure, or at + 0·007° C. when under the pressure of its saturated vapour, *viz.* 4·579 mm. Hg, this latter temperature must mark the upper limit of the sublimation curve on a temperature-pressure diagram. Existence of ice, *i.e. ordinary ice*, above + 0·007° C. has never been observed. On the other hand, it is possible to super-cool liquid water below 0·007° C. (the temperature at which liquid water under its own vapour pressure should solidify). This *metastable* state of the liquid—vapour system, is represented in the diagram by the dotted line OA′, which it is important to note is an unbroken continuation of the stable vapour pressure curve OA. Note particularly that OA′ lies *above* OB. That is at any given temperature below the point O, the vapour pressure over the super-cooled water, which is the unstable phase, is greater than the vapour pressure over the stable phase, solid ice. We have already seen, on thermodynamic grounds, that this must be so (this Vol., Chap. IV.).

The System: Liquid water—ice (ordinary form).

A one-component system consisting of these two phases is also bivariant. The series of equilibrium states, corresponding, say, to a series of pressure values, is represented by the line OC. The line OC is the freezing-point curve. The upper limit as far as temperature is concerned is + 0·007° C. since ordinary ice cannot exist above this temperature. By increasing the pressure on ice alone, we know that it will melt. This means that if we have ice and water together, under a certain pressure, say the pressure of saturated vapour, there will be an equilibrium at O, and on arbitrarily increasing the pressure it will be necessary to lower the temperature of the system in order to keep the ice as a permanent part of it. On the basis of the Le Chatelier-Braun principle, the change of freezing temperature (*i.e.* equilibrium temperature) with pressure is extremely small, as one would expect from the small volume change that accompanies fusion, and hence the line OC is very steep.

The System: Ordinary ice—liquid water—vapour.

This system consists of three phases, and since there is only one component $f = 0$, *i.e.* the system is invariant or has no degrees of freedom. This means that we cannot fix any condition (such as temperature and pressure) arbitrarily. This system can only permanently exist at a single point on the temperature-pressure diagram. This equilibrium point is O, which corresponds to the conditions—

$$T = + 0{\cdot}0076^\circ \text{ C.}, \quad P = 4{\cdot}579 \text{ mm. mercury.}$$

If we attempt to alter either T or P, one of the phases will disappear. Thus on raising the temperature to the slightest extent the ice phase will vanish, and the system will again be in equilibrium on the OA curve, infinitely close to O. On lowering the temperature the vapour and the liquid phase will both tend to disappear. Which will disappear first depends on the absolute amounts of each. If the vapour disappears first the system will again cease changing, *i.e.* will come into an equilibrium position on the OC curve at a point infinitely close to O. If the liquid phase disappears[1] first (*i.e.* becomes solid) the system will be on the curve OB. The point O at which three phases are in equilibrium is called a *triple point.*

The Hypothetical Case: Two forms of ice[2]—liquid water—vapour.

This being a one-component system $n = 1$
There are four phases $r = 4$
$\therefore f = n - r + 2 = 1 - 4 + 2 = -1.$

[1] We are here leaving out of account meta-stable conditions, which do not represent true equilibrium states.

[2] See later Tammann and Bridgman's work on the various forms of ice.

Such a system would possess a negative value for the degrees of freedom. To have less than zero degrees of freedom is unrealisable. We can therefore infer, on the basis of the Phase Rule, that it is an impossibility to have a *stable* system consisting of only one component in more than three phases. If such a system be set up, one of the phases will commence to disappear no matter what values we give to the temperature and pressure. This is a striking instance of the usefulness of the Phase Rule as a guide to the chemical behaviour of heterogeneous systems.

Various Forms of Ice and the Corresponding Systems which can be formed thereby.

So far we have spoken of ice as "ordinary ice," as though there were only one crystalline form or modification of water in the solid state. Tammann,[1] however, has found three crystalline forms, *i.e.* three different phases in which solid H_2O can exist. Ordinary ice is called by him ice I., the other varieties being ice II., and ice III. These latter varieties can be reached at low temperatures and very high pressures. According to the Phase Rule one may expect to have a number of systems in addition to those already discussed. Of these Tammann found the following *Invariant Systems* :—

liquid water—ice I.—ice III.
ice I.—ice II.—ice III.

Each of these systems exists in equilibrium only at one point characteristic of the phases present. Hence beside the point O (Fig. 36), Tammann's results show the existence of two other triple points.

Univariant Systems :—

liquid water—ice III.
ice I.—ice II.
ice I.—ice III.
ice II.—ice III.

These would be represented by *lines* in a T.P. diagram.

Bivariant Systems :—

ice II.
ice III.

Each of these bivariant systems is represented by an *area* on the T.P. diagram, *i.e.* we can alter both temperature and pressure simultaneously within limits, without causing the phase to disappear. The work of Tammann has recently been extended by the investigation of the H_2O system at low temperatures and very high pressures by P. W. Bridgman (*Proc. Amer. Acad.*, **47**, 441, 1912). Tammann, working up

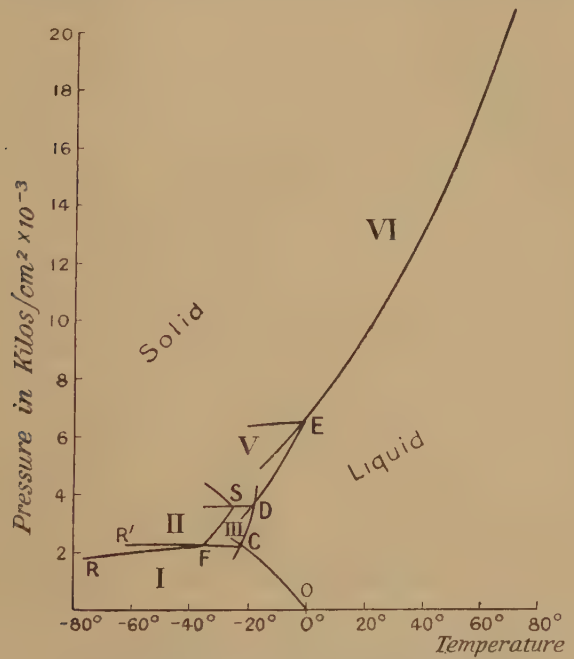
[1] Tammann, *Annal der Physik*, [4], 2, 1424, 1900.

to 3500 kilograms per square centimeter pressure, had shown the existence of three different forms of ice; Bridgman, by working up to 20,500 kilos per square centimeter, has succeeded in demonstrating the existence of yet two other stable forms, making five definite crystalline varieties of ice. All these forms, with the exception of ordinary ice (ice I.) are *denser* than that of water. Bridgman was able to locate five of the six[1] possible triple points (three phases in equilibrium) and ten out of the eleven possible transition lines (two phases in equilibrium) have been followed. The sixth triple point and the eleventh equilibrium line lie at the temperatures so low and pressures so high that the slowness of the reaction, *i.e.* the rate of transformation of one variety into another, makes them practically impossible to determine. The passage of one phase into another we speak of as "transition". The lines OA, OB, OC, in the figure 36, are transition lines. The triple point, such as O, is called the "transition point". The method of determining the actual existence of new substances, such as the new crystalline forms of ice, is to try and map out on a T and P diagram, the direction and length of transition lines and determine the location of transition points. In this way we can visualise the range of stable existence as regards T and P of each phase in contact with other phases. Such a diagram given in the figure (Fig. 37) has been mapped out by Bridgman, showing the equilibrium relations of the five different forms of ice and the liquid. The various forms of ice are denoted by the symbols ice, I., II., III., V., and VI., respectively. The new forms discovered by Bridgman are ice V. and ice VI. The absence of the term ice IV. is due to the fact that although Tammann obtained some evidence (*Zeit. physik. Chem.*, **72**, 609, 1910) for such a modification, there still remains considerable doubt in regard to its existence. If later it should be found, space is left for it on the above scheme of nomenclature. (For a discussion of ice IV., see Bridgman's paper, *l.c.*, pp. 527 *seq.*)

It will, perhaps, make the diagram more easily understood if we imagine ourselves following out the behaviour of the H_2O system, starting from the ordinary triple point O. The observer is supposed to be able to distinguish by sight simply the different forms of ice, even though the actual enclosing vessel is necessarily hard steel to withstand the high pressure impressed upon the system by means of a steel plunger. If the pressure at O be increased, the vapour phase may be caused to disappear, and we are left with the liquid—ice I. system. By continuously increasing the pressure and suitably lowering the temperature we can keep these two phases in equilibrium, *i.e.* we can pass through a consecutive series of equilibrium points represented by the curve OC. This curve is a continuous one having the shape indicated until we reach the pressure of 2115 kilos per square centimeter and the temperature -22° C., at which point there is a sharp discontinuity indicated by the point C. The system will now be "seen" to consist of three

[1] Six in addition to the triple point O (Fig. 36) where ice I.—liquid—vapour coexist in equilibrium.

phases, ice I.—ice III. and liquid. Point C is therefore a triple point. If we now further increase the pressure, and at the same time *raise* the temperature very slightly, ice I. will disappear and we are left with ice III. and liquid. By further increasing the pressure these two phases can be kept in equilibrium by suitably raising the temperature, and in this way we can pass along the line CD with continuously increasing pressure. At D the CD line is broken sharply and another solid phase makes its appearance, namely, ice V., point D being the triple point



Equilibrium Diagram between liquid water & the 5 solid modifications of ice

FIG. 37.

corresponding to the co-existence of ice III., ice V. and liquid. The pressure is 3530 kilos per square centimeter and the temperature – 17° C. On still further increasing the pressure and *raising* the temperature again slightly, ice III. can be made to disappear, and we may pass along the curve DE which represents the equilibrium line of ice V. and liquid. At the point E (pressure 6380 kilos per square centimeter, temperature + 0·16° C.) the curve DE is broken, the phase ice VI. making its appearance, the point E being the triple point for the three phases, ice V., ice VI., and liquid. On increasing the pressure it is possible to follow the equilibrium stages of ice VI. in contact with

liquid. This curve has been traced without showing any break up to pressures of the order of 20,000 kilos per square centimeter, the limit of Bridgman's pressure apparatus, and temperature about + 80° C., without any new phase making its appearance. These results show that it is actually possible to have H_2O in the solid form in equilibrium with liquid at a temperature as high as + 80° C. The solid here is, however, not ordinary ice but a new modification ice VI.

Now let us return to the triple point C. Let us increase the pressure, only to an extremely slight extent, and let us lower the temperature to a suitable extent (instead of raising it). The liquid phase will now disappear and the system will consist of ice I. and ice III., the equilibrium between these two states being followed by lowering the temperature and suitably adjusting the pressure. In this way we pass along a continuous curve CF which shows a break (*i.e.* a sudden change in direction) at F, at which point a new solid form is produced, namely, ice II. F is the triple point, ice III., ice II., ice I. (pressure = 2170 kilos per square centimeter, temperature − 34·7° C.). By still further lowering the temperature, ice III. can be caused to disappear, the remaining phases, ice II. and ice I., being kept in equilibrium by slightly *lowering* the pressure, *i.e.* we pass along the line FR. Note that the line FR′ is the meta-stable equilibrium line between ice I. and ice III. that is, we have passed the point F at which ice II. should appear, but owing to the slowness of reaction in solid phases, especially at low temperatures, we have super-cooling of the ice III. phase. The prolongation of lines through the other triple points represent the same phenomena also taking place. This phenomena of "suspended transformation" is of quite frequent occurrence, and, as one might expect, it greatly increases the difficulty of accurately determining the true transition point (in the present case a triple point). In the case of two solid phases, the transition point can be over-stepped in both directions. In the case of the transition point of a solid and liquid together the liquid can be super-cooled easily, but no case yet has been recorded in which the solid has been heated above the triple point without passing into the liquid state. Suspended transformation is therefore limited to one direction. This is the only distinction between a solid—solid transition point and a solid—liquid melting point. Again, if we imagine ourselves at the point F and raise the pressure, we can cause ice I. to disappear and ice II. and ice III. to remain in equilibrium by *raising* the temperature. In this way we pass from F to S, at which point ice V. makes its appearance (pressure 3510 kilos per square centimeter, temperature − 24·3° C.), and on raising the temperature we can cause ice II. to disappear, and by suitably increasing the pressure to a very slight extent we can pass along SD to the triple point D already described. The following table summarises the T.P. data already given for all the triple points of the H_2O system which have been experimentally realised :—

Phases.	Position on Diagram.	Temperature.	Pressure.
Ice I.—liquid—vapour . .	O	+ 0·0076° C.	4·579 mm. Hg.
,, ,, ice III. . .	C	− 22° C.	2115 kilos/cm.^{2}
Ice III.—liquid—ice V. .	D	− 17° C.	3530 ,,
Ice V.—liquid—ice VI. . .	E	+ 0·16° C.	6380 ,,
Ice I.—ice II.—ice III. . .	F	− 34·7° C.	2170 ,,
Ice II.—ice III.—ice V. .	S	− 24·3° C.	3510 ,,

It will be observed that the field of existence of ice II. is bounded by ice I., ice III., and ice V. It is impossible to get ice II. in contact equilibrium with liquid under any temperature or pressure values whatsoever. Ice II. does not melt, *i.e.* ice II. cannot be brought into equilibrium with the liquid form. Starting with some ice II., on raising the temperature we transform it into ice III., unless indeed the temperature has been raised too quickly and we obtain super-heated ice II., which might conceivably "melt". The system, however, would not be an equilibrium one. It is thus impossible to predict (apart from experiment) as to *how many* triple points a given number of phases may give rise. We must find out by experiment something about the slopes of the transition lines between pairs of phases in the case of one-component systems such as H_2O, before we are able to state the probable sets of triple points. If we are able to measure the specific volumes of two phases separately we can foretell by applying the Le Chatelier-Braun principle what will be the direction of the slope of the equilibrium curve on increasing the pressure, for under these conditions, according to this principle, the system will tend to transform itself into that occupying the least volume. To prevent, therefore, the total disappearance of one of the phases we have to alter some other condition of the system, *i.e.* the temperature. It will be observed that in the case of the forms ice III., ice V., and ice VI., increase of pressure *raises* the freezing point, *i.e.* the behaviour is the reverse of ice I. From the Le Chatelier-Braun principle we see that this is due to the fact that the density of these other forms of ice is greater than that of the liquid in equilibrium. The phenomenon of "regelation" can occur therefore only with ice I.

Of course in following out the diagram, as has been done in the preceding pages, we are obviously carrying out a purely imaginary process. The actual slopes of the lines, and the discontinuities indicating the points at which new phases appear, are determined by observing the change in some physical property of the system (such as the *volume*) under varying conditions of temperature and pressure. Bridgman, following Tamman's method, determined what was virtually the compressibility of the H_2O system under various conditions, the system being enclosed in a thick-walled steel piezometer. In other cases other properties may be employed. These will be mentioned in connection with the particular system followed. The more important may be summarised here:—

I. Measurement of change in volume by means of a dilatometer or piezometer.

II. Measurement of vapour pressure (Bremer-Frowein tensimeter).

III. Measurement of solubility.

IV. Thermo-analytical method.

V. Optical method.

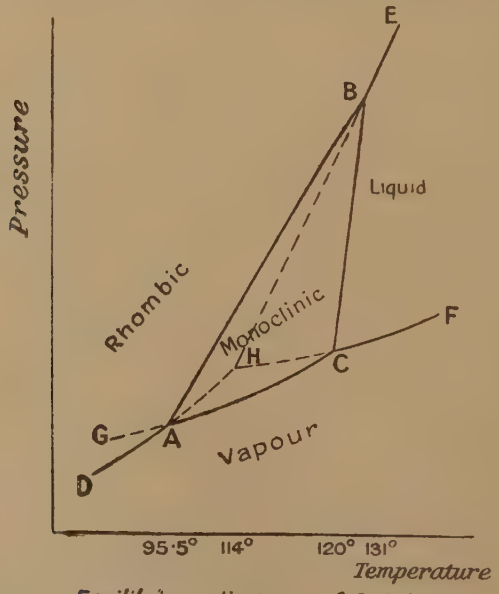
VI. Electrical methods (measurements of conductivity and electromotive force).

VII. Measurement of viscosity (Dunstan and Langton, *Trans. Chem. Soc.*, **101**, 418, 1912).

An account of most of these methods is given in the appendix to Findlay's Phase Rule.

ONE-COMPONENT SYSTEMS (*continued*).—COMPONENT: SULPHUR $(S)_n$.

It is a fact familiar to every chemist that sulphur can exist in two crystalline modifications, rhombic and monoclinic, as well as in the liquid and gaseous forms. The conditions of equilibrium of the various



Equilibrium diagram of Sulphur
Two solid phases–liquid–vapour.

FIG. 38.

phases of this one-component system, can be represented by the usual P.T. diagram given in the figure (Fig. 38). In this case, as in the last, the equilibrium lines and points have been determined by measurements of the change of volume, with changes in temperature and pressure.

Experiment has shown[1] that if we start with solid rhombic sulphur, on heating it rapidly it melts at a temperature 114° C. (point H). If, however, we keep rhombic sulphur heated at any temperature between 96° C. and 114° C. it will be found to have become transformed into monoclinic sulphur, which will now melt at 120° C. This rather anomalous behaviour is easily explained when we study the system systematically, from the standpoint of the Phase Rule. Thus Reicher showed that at a temperature 95·5° C., and under a certain pressure, namely, the pressure of the saturated sulphur vapour, the rhombic form passes into the monoclinic. This is represented by the point A. This is a triple point corresponding to the stable coexistence of the three phases, solid rhombic—solid monoclinic—vapour. According to the Phase Rule, since the system only consists of one component we cannot get more than three phases to remain together in *equilibrium*. If at the point A we compress the system until the vapour phase entirely disappears, it will be found that on further increasing the pressure it is necessary to raise the temperature in order to keep both rhombic and monoclinic present together. We thus pass along the line AB. When the temperature has reached the value 151° C., and the pressure 1288 atmospheres, liquid sulphur may be brought into contact with the two solid phases and the system is in equilibrium. This is the triple point B, at which monoclinic, rhombic, and liquid can coexist. This is taken as the *true* melting point of rhombic sulphur. If we still further increase the pressure, the monoclinic form will entirely disappear, and we can keep rhombic and liquid present together by suitably raising the temperature. In this way we pass along the line BE. Of course each point on this line is a melting point of rhombic under the given pressure. The point B corresponds to the lowest temperature and pressure at which rhombic will remain stable in the presence of liquid. Again returning to the point A, if we raised the temperature very slowly without altering the pressure, it will be found that rhombic disappears, and we are left with monoclinic in the presence of vapour. The point A is therefore the "transition point" of rhombic into monoclinic. To keep the monoclinic and vapour permanently present together, as we raise the temperature the pressure must likewise be raised. The system does this automatically by the increase in its vapour pressure. We thus pass along AC. At the point C the monoclinic melts. At C therefore we have another triple point, monoclinic—liquid—vapour. This is the temperature 120° C., the true melting point of monoclinic sulphur. On further raising the temperature the monoclinic disappears and we pass along CF, which is the "vapour pressure curve" or equilibrium curve of liquid sulphur in contact with vapour. If at the point C we had compressed the system so as to make the vapour phase disappear, and then had further increased the pressure, it would be found necessary to *raise* the temperature in order to keep monoclinic and liquid present together. By successively increasing the pressure and temperature we can pass along the line CB, which represents the

[1] More accurate data are considered later.

melting point of monoclinic under various pressures. At B we can add some rhombic, and the three phases will be found to be in equilibrium as already mentioned. We have so far dealt with three stable triple points, viz. A, B, and C, and with five stable equilibrium lines AB, BE, AC, CF, CB. There is yet another stable equilibrium line, namely AD. If we start again at A with the three phases, vapour, monoclinic and rhombic, and lower the temperature, it will be found that the monoclinic is transformed completely into rhombic, and the rhombic and vapour can be kept in equilibrium at a series of lower temperatures by suitably lowering the pressure (*i.e.* an automatic effect of the system itself by the lowering of its own vapour pressure). In this way we pass along AD. Besides these transformations of stable forms, it is also possible to observe unstable equilibrium points. Thus the point H (which can be reached by rapidly heating *rhombic* sulphur until it melts) is the unstable triple point corresponding to the three phases, rhombic, liquid, and vapour. The point H is obtained by producing the *stable* rhombic—vapour line AD, the stable liquid—vapour line CF, and the stable rhombic—liquid line BE. In heating rhombic quickly in presence of its vapour we start along DA, and instead of rhombic changing into the stable monoclinic variety at A, the system rhombic—vapour can be carried along the line AH to H, at which point liquid makes its appearance. Similarly, if we had started somewhere on the line BE with rhombic and liquid in equilibrium, and lowered the temperature and the pressure correspondingly we would reach B, at which point monoclinic should appear. If the temperature and pressure changes are rapid, however, we can carry the system rhombic—liquid down to much lower temperatures and pressures, namely, along BH to H. In a similar manner, we can super-cool the liquid at C so that the liquid vapour system, which has been passing along FC can be made to pass as far as H. That H represents an unstable state is shown by the fact that if we reach H, by any of the routes mentioned, and keep the system (rhombic—liquid—vapour) in contact for a sufficient time, the system will completely transform itself into monoclinic and vapour, the path followed being a vertical line down until the AC curve is reached at the temperature of H, and the vapour pressure corresponding to this temperature. As regards the stability of monoclinic sulphur, it will be seen from the figure that it is limited on all sides. That is, it can only exist as a stable phase within certain fixed temperature and pressure limits. The line GA represents the unstable equilibrium curve of monoclinic—vapour system. The system ought, on being cooled at A, to change into rhombic and follow the line AD. That AG is unstable is shown by the fact that on keeping monoclinic in contact with vapour at a temperature corresponding to some point on AG the system will entirely transform itself into rhombic and vapour. Its path will be represented by a vertical line downwards (at constant temperature) until the vapour pressure takes on the value corresponding to that of the curve AD at the same temperature. In the cases of the majority of substances it will be observed that melting of the solid eventually occurred on raising

the temperature sufficiently, and this liquid could be entirely vaporised on further raising the temperature. It may happen, however, that the complete transition from solid to gas (*i.e.* sublimation) on raising the temperature, takes place without the appearance of the liquid phase. If the vapour pressure of a substance is greater than the atmospheric pressure at any temperature below the point of fusion, then the substance will sublime without melting when heated in an open vessel, and fusion will only be possible at a pressure higher than atmospheric. Red phosphorus and arsenic are instances of this behaviour.

The component sulphur is thus capable of giving rise to the following systems:—

Invariant systems: Triple points.

Stable	A	corresponding to rhombic—monoclinic—vapour.
	B	„ rhombic—monoclinic—liquid.
	C	„ monoclinic—liquid—vapour.
Unstable	H	„ rhombic—liquid—vapour.

Univariant systems: Curves.

Stable	AD	corresponding to rhombic—vapour.
	AB	„ rhombic—monoclinic.
	AC	„ monoclinic—vapour.
	CF	„ liquid—vapour.
	CB	„ monoclinic—liquid.
	BE	„ rhombic—liquid.
Unstable	AG	„ monoclinic—vapour.
	AH	„ rhombic—vapour.
	HC	„ liquid—vapour.
	BH	„ rhombic—liquid.

Bivariant systems: Areas.

Stable	Space to the left of DABE—rhombic.
	„ „ right of FCBE—liquid.
	Space below DACF—vapour.
	Area ABC—monoclinic.

It will be observed that the Phase Rule predicts that four phases, such as rhombic, monoclinic, liquid, vapour, cannot possibly coexist in equilibrium since there is only one component, and this would make f negative. As regards the slope of the lines such as AB, AC, BC, the principle of Le Chatelier-Braun will allow us to predict the general trend if we know beforehand the densities or specific volumes of the phases. Thus the curve AB (monoclinic—rhombic) slopes to the right on increasing the pressure. If we start with any point on AB and increase the pressure, keeping the temperature constant, it will be found that the monoclinic will change into rhombic, *i.e.* we will pass along a vertical line, which takes us right into the field of rhombic. This must

mean that the specific volume of rhombic is less than that of monoclinic. A similar relation holds for the transformation of monoclinic into liquid (BC), the slope of the curve showing that the monoclinic has the smaller specific volume than the liquid, *i.e.* the reverse of the case ordinary ice I. and water.[1]

ONE-COMPONENT SYSTEMS (*continued*).—THE COMPONENT TIN.

Tin is known to exist in two solid forms, "white" and "grey," as well as in the liquid and vapour. We thus have a case analogous to that of sulphur. The interesting point is the determination of the transition point, white to grey (*i.e.* the triple point, white—grey—vapour), which can be effected in this case by an electrical method. If we set up a cell containing an aqueous solution of tin salt, one electrode being white tin, the other grey tin, in general an e.m.f. will be given by the cell. This is due to the fact that the electrodes are not electromotively identical, *i.e.* they do not possess the same solution pressures. The two electrodes not being identical, there is a tendency for a chemical reaction of some sort to occur, in this case the transformation of white tin into grey tin, or *vice versâ*. The fact that substances are not in equilibrium with one another is always manifested by the existence of an e.m.f., if the nature of the system allows a cell to be set up. This is dealt with at greater length in the chapter on "Affinity". If, however, white and grey tin were in equilibrium, *no* e.m.f. would be produced. At the transition point this equilibrium is obtained, and hence the transition point will be that temperature at which the cell gives no e.m.f. By placing the cell in a bath, the temperature of which can be altered, the transition point can then be accurately determined. Cohen and van Eyk found it to be + 20° C. Below this temperature grey tin is stable. The investigation of the transformations of tin, and the causes of the phenomenon known as "tin pest," has been made in particular by Cohen and his collaborators (*cf. Zeitsch. physik. Chem.*, **30**, 601, 1899, and several papers in recent years).

Besides the transition of grey tin into white tin, the component tin shows another transition at a very much higher temperature. Ordinary white tin is tetragonal, but at a temperature of about 203° C., A. Smits and H. l. de Leeuw (*Proc. k. Akad. Wetensch.*, Amsterdam, 1912, **15**, 676) have shown that there is a transformation into a brittle form, crystallising in the rhombic system. It is difficult to bring this change about, but it can be catalysed by the addition of small quantities of mercury. This, however, has the serious disadvantage of depressing the transition temperature. This transition was observed by dilatometric measurements, not by electromotive force.

[1] The system sulphur is studied further on, p. 298 *seq.*

Two-Component Systems.

Before taking up the behaviour of any particular system in detail it is necessary to consider some of the phenomena associated with the physical properties of compounds and mixtures (liquid and solid solutions), and to see how these properties (such as fusion and solidification temperatures, boiling points, vaporisation, and solubility) are able to afford us valuable information regarding the *chemical* changes which a system may undergo.

Thus consider the two-component system H_2O—NaCl, the special case being a dilute solution of salt in water at a given temperature. Let us suppose the temperature of the solution is lowered. At a given temperature *ice* (solid H_2O ice I.) will make its appearance. This is the so-called freezing point of the solution. It will be observed, however, that this is not a "*sharp* freezing or melting point," *i.e.* the solution as a whole cannot be made to solidify at the temperature at which ice first made its appearance. It is necessary to go on lowering the temperature, more and more ice being therefore precipitated. Analysis will show that in this case (as in the majority of inorganic salts and water) the solid which comes out is pure ice. There is no salt present in the solid phase. As the solid phase increases in bulk the solution naturally increases in concentration (in respect of the salt), and we already know that a concentrated solution freezes at a lower temperature than a dilute one. This change in the concentration of the salt is the cause of *the progressive lowering of freezing point*, which any solution of this nature will show. This lowering will not, however, go on without limit. A temperature is finally reached, at which the salt has reached its limit of solubility in the liquid, and both solid salt and ice are precipitated, in the same proportion as they existed in the solution. At this temperature the whole system will go solid. This therefore represents the lowest possible value for the "freezing point" of the solution. It is called the *cryohydric* or *eutectic point* or *temperature*. Microscopic analysis will show that the cryohydric solid is in this case *heterogeneous*, *i.e.* it consists of ice crystals lying side by side with salt crystals, but there is no solid solution formed. The salt crystals are, however, in this case not anhydrous salt, but salt in the form of the dihydrate, $NaCl \cdot 2H_2O$. The behaviour of the system is best shown by the aid of the diagram (Fig. 39). It will be seen that the cryohydric point C is simply the point at which the solubility curve of the salt DC cuts the freezing point curve of the solution. The existence of such cryohydric points is of immense importance in connection with the efficiency of freezing mixtures. No freezing mixture can cool itself down below the cryohydric point of the particular solvent and solute employed. [This automatic cooling effect is, of course, of different origin to the external cooling we have supposed in the above. In freezing mixtures, say of ice and common salt, the salt dissolves in some of the liquid (moisture) which always adheres to the ice crystals. This solution and the ice are not, however, in equilibrium, say, at 0° C,

There would only be equilibrium if the temperature were lower. Some of the ice therefore melts, and to do this the latent heat of fusion has to be supplied by the system itself, which thereby cools. Further salt now dissolves and the same process is repeated, with the result that the temperature falls still further. The temperature can never fall, however, below the cryohydric point, since at this temperature the solution being saturated the salt has no further tendency to dissolve.] The close analogy between "freezing point" curves and "solubility curves" will be clear from the figure. In the case which we have considered we started with a solution, the composition of which (in respect of salt) lay to the left of C, and at room temperature, say. If, on the other hand, we had started with a concentrated solution of salt (to the right of C), and at room temperature, and had cooled this down, at a certain temperature solid salt, either anhydrous or in the dihydrate form, would have precipitated itself. This can be equally regarded as the freezing point of the solution, or the solubility point (temperature), though it is more usual to regard it as the latter. In this case also, the solution would not become entirely solid at the temperature at which salt first appeared, but as the temperature was lowered more and more salt would be precipitated until the temperature C was again reached, and ice as well as salt is simultaneously precipitated. Actual analysis of the solid phase which separates out from concentrated solutions of salt has shown that above the temperature + 0·15° C. the solid is anhydrous NaCl, below this temperature the solid is the compound $NaCl \cdot 2H_2O$. The temperature 0·15° C. is therefore the transition point of the dihydrate into the anhydrous form. Above this temperature we say that the anhydrous salt is the stable form, below this temperature the dihydrate is stable. It will be observed that the relative slope of the two curves, CD and DB, is in agreement with the generalisation which we have reached on thermodynamical grounds, *viz.* that at a given temperature the unstable form has a greater solubility than the stable form. Thus, suppose the line CD produced upwards into the region where the dihydrate is unstable. It will be seen, on selecting any temperature and drawing vertical lines downward from each curve to the concentration axis, that at one and the same temperature the solubility of the dihydrate (if it could be got into this position at all) is greater than that of the anhydrous salt. Similarly at temperatures below D, the anhydrous salt (which is now unstable) has a greater solubility than the dihydrate.

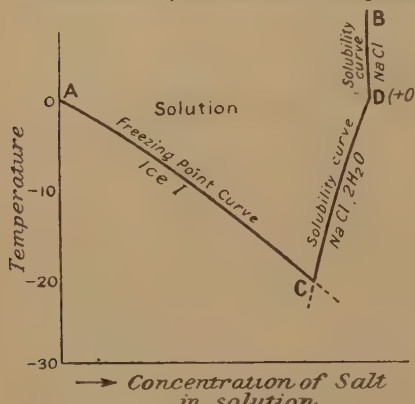


FIG. 39.

Formation of Solid Solutions.

In the above case the two constituents are precipitated separately (at the cryohydric point together, but heterogeneously). In some cases both constituents are precipitated simultaneously (at all "freezing points"), and the solid is a homogeneous solid solution. The formation of solid solutions, in which the components are mutually miscible in all proportions, can give rise to three types of curves, the first two of which are important. In the first type the freezing or melting points of the mixture lie between the freezing points of the two pure constituents. This is illustrated in the accompanying diagram (Fig. 40), which shows the behaviour of mixtures of chloro-cinnamic-aldehyde and bromo-cinnamic-aldehyde, or by alloys of gold and platinum. The freezing point of the pure chloro-compound is 31·22° C., that of the

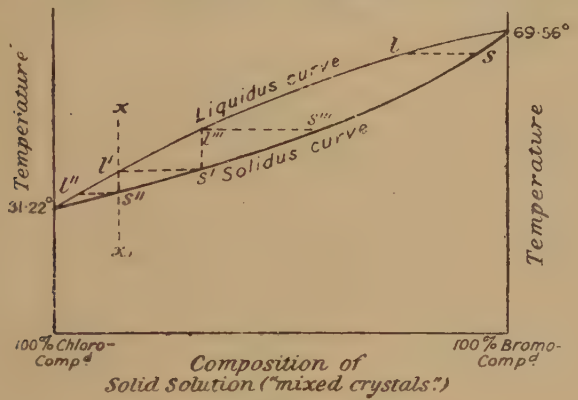


FIG. 40.

bromo-compound is 69·56° C. Suppose a little chloro-compound is added to the pure bromo-compound. The freezing point is lowered. In those cases in which the "solute" crystallises out with the solvent, the lowering of freezing point $-\Delta T$ is given by the expression—

$$-\Delta T = \frac{RT^2(x_1 - x_2)}{L},$$

where x_1 is the concentration of solute in the liquid phase, and x_2 the concentration in the solid. In order that a *lowering* of freezing point may take place it is necessary that $x_1 > x_2$, *i.e.* that the concentration of the chloro-compound shall be greater in the liquid solution than it is in the solid. To represent the behaviour of the system consisting of liquid and solid solutions, it is thus necessary to have TWO curves, *which in certain cases may, indeed, lie very close together but can never be identical.*[1] One curve gives the composition of the liquid solution, and

[1] Except in the special case in which the melting points of both constituents are identical, and then the line is horizontal on a Tx diagram similar to that given.

is known as the liquidus curve; the other gives the composition of the corresponding solid solutions, and is known as the solidus curve. In the above case the upper curve gives the composition of the liquid solution, the lower that of the solid solution. The impossibility of both curves being identical, except at the limits, is evident from a consideration of the above formula, for identity of the two curves would mean identity in composition of the two phases, and this would mean that $x_1 = x_2$ and therefore $- \Delta T = 0$. That is, the addition of the second component would have no effect on the freezing point, which is evidently quite unthinkable since the pure substances have quite different melting points, and we must be able to pass from one extreme to the other. The problem of the relative position of the solidus and liquidus curves is solved by means of the thermodynamical equation given. Stated in general terms the conclusion is as follows:—

"*At any given temperature the concentration of that component, by the addition of which the freezing point is depressed, is greater in the liquid than in the solid phase; or conversely, the concentration of that component by the addition of which the freezing point is raised is greater in the solid than in the liquid phase.*" The comparison of the concentration of the two phases must, of course, be made at the same temperature. This is represented, for different temperatures, at different parts of the curve, by the lines *ls*, *l's'*, and *l''s''*, etc.

It will be evident that in a case such as that just considered the freezing point of the solution at any composition (except the two extreme points) *will not be sharp, i.e.* the system as a whole cannot be solidified at one temperature, there being instead a progressive change of freezing point.[1] This is due to the fact that at no point is the composition of solid and liquid identical, except, of course, in the case of each pure substance, at the ends of the curve. Referring to the preceding diagram, suppose that the system under examination is a liquid solution of the two components at the composition and temperature denoted by the point *x*. Suppose the temperature is lowered, the system begins to pass along the vertical line *xx'*. On reaching the point *l'*, some solid is deposited, the solid having the composition *s'*. On lowering the temperature further, solid comes out of solution, the composition of the *solid* phase passing along *s's''*, the composition of the liquid being simultaneously represented by a series of points on the line *l'l''*. If the temperature be still further lowered, the system as a whole may go solid. There is thus a greater or smaller temperature interval, *l's''* "the crystallisation interval," which must be passed through between the first appearance of solid and the final complete solidification. It should be noted that in order to have the solid phase homogeneous as regards *concentration* of the components it is necessary to allow the operation of cooling to go on very slowly, for as the composition of the freshly de-

[1] Ordinary solutions, such as salt and water, exhibit the same phenomenon (for the same reason). The "freezing point" of such a solution is therefore the temperature at which a very small quantity of some constituent begins to come out in the solid form.

posited solid is continuously changing (along $s's''$) there must be diffusion in the solid itself to give an average composition. To bring this diffusion about it is usual to heat the solid to a temperature somewhat below its melting point. This is known in alloy work as "annealing" (*cf.* Desch, *Metallography*, pp. 46 *seq.*). Fractional crystallisation of mixed crystals (as solid solutions are sometimes termed) can be effected by separating off the solid mass which appears at s', say, remelting this, and allowing it to deposit other crystals represented by s''', separating these in turn and again melting and recrystallising. In these processes the solid is gradually becoming richer in the bromo-compound (taking the particular case studied). Theoretically, however, the separation can never be complete.

The second type of behaviour exhibited by solid solutions may be illustrated by the system mercuric iodide and mercuric bromide, which are also capable of forming solid solutions with one another in all proportions. The behaviour of this system is, however, different from that already considered, though here also, as we shall see, there is no compound formed. Mercuric iodide melts at 255° C., mercuric bromide at 236·5° C. The melting point of mixtures of these two, however, does *not* lie on lines connecting these two temperatures. Instead the behaviour is shown in the diagram (Fig. 41.), which is a temperature concentration diagram. Analysis shows that the composition of the solid and liquid forms in equilibrium with one another (at a given freezing point) are not the same, except at one temperature, namely, C, the lowest temperature at which the system formed from these two components can be made to melt or to freeze. The composition of both solid (s) and liquid (l) are shown. Suppose we have chosen a mixture of 75 per cent. mercuric iodide, and 25 per cent. mercuric bromide, and have heated it until it is completely liquid. Now begin lowering the temperature, thereby allowing some to resolidify, and analyse both phases. It will be found that the liquid has the composition denoted by l and the solid (which is a *homogeneous* solid solution) has the composition denoted by s. It is impossible to cause the whole liquid to solidify at this temperature, for the solid being richer in iodide than the solution the process of solidification entails the gradual impoverishment of the solution as regards HgI_2, and the freezing point falls until we reach s''. We here regard the HgI_2 as the "solvent," the $HgBr_2$ as the solute (because there happens to be much more HgI_2 present), though of course the terms are always interchangeable. At the point C the solid separating is identical in composition with the solution, and the whole system can solidify sharply. This only differs from the cryohydric point in the ice-salt case, in the fact that in the present system the point C is a point on a *continuous* curve, and the solid is a *homogeneous* solution of both components. In the above cases there is no evidence of the formation of a true compound. Further, in these cases no melting point was observed *higher* than that of either pure constituent; nor, indeed, was a curve obtained having a portion *concave* (towards the concentration axis). This type of curve is obtained

in the case of *solid solutions* of optical isomerides, namely, *d* and *l* carvoxime, in which no compound is formed although the curve passes through a maximum, *i.e.* has a melting point higher than that of either single component. This curve is shown in the figure (Fig. 42). The composition of the solid and liquid phases are different except at the

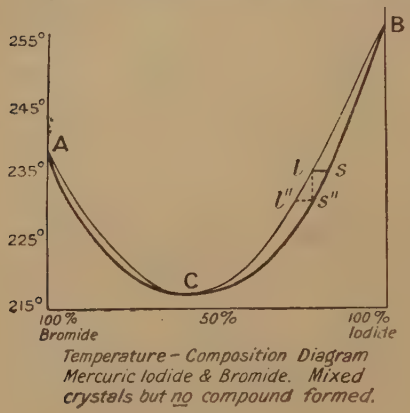


FIG. 41.

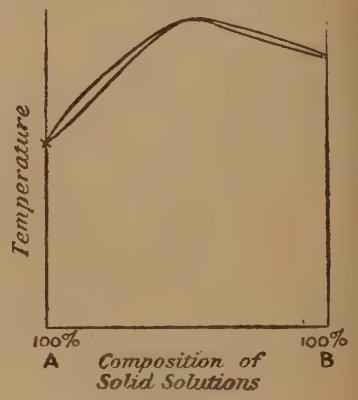


FIG. 42.

maximum point. It will be observed that in *this case there are no eutectics* to either side of the maximum. Desch states that in alloys this type of curve is never found. The significance of the absence of eutectic points on either side of the maximum will be clear from the consideration in the next paragraph of the system α-naphthylamine and phenol which will now be discussed.

Formation of Compounds.

In the case of α-naphthylamine and phenol *no solid solution* is formed, but instead a *true compound* of the two components (J. C. Philip, *Trans. Chem. Soc.*, **83**, 821, 1903), *cf.* Fig. 43. Phenol melts at 40·4° C., and α-naphthylamine at 48·3° C. On adding some of the amine to liquid phenol, the freezing point of the solution is lowered, and we can then pass along AC by adding successive amounts of the amine. The solid which separates is pure phenol until the point C is reached, at which the whole system may be caused to solidify. This must be a eutectic point, some other solid besides the phenol having evidently separated out. Analysis shows the presence of both phenol and the amine, but this leaves us in doubt as to what the solid is. The case may only be analogous to that of ice and salt. On further addition of the amine the temperature of equilibrium between solid and liquid phases *rises*. At D the curve passes through a *maximum* (28·8° C.), and on further addition of amine again falls. Analysis shows that at D the composition of the solid and liquid are identical (as was also the case at C). Further, at D this composition of both liquid and solid is

exactly given by the formula C_6H_5OH, $C_{10}H_7NH_2$. By adding amine we finally reach another point E, at which the system can be solidified entirely without change of temperature. Starting with pure amine and adding phenol, we can obtain a series of freezing points along BE. E is the second eutectic, the prolongation of the lines AC and BE, below C and E respectively, denote meta-stable conditions of the system, which in this case can be reached owing to the slow rate of transformation from one form to another. Now we know that the addition of any foreign substance will lower the freezing point of a pure substance. This is what has happened at D. In fact, if we assume the existence of a compound consisting of phenol and α-naphthylamine in equi-molecular proportions, the shape of the curve ACDEB is what we would expect. D is the melting point of the compound, and it can be lowered either by the addition of phenol *or* of α-naphthylamine. In this way we can account for the fall on both sides to C and E respectively.

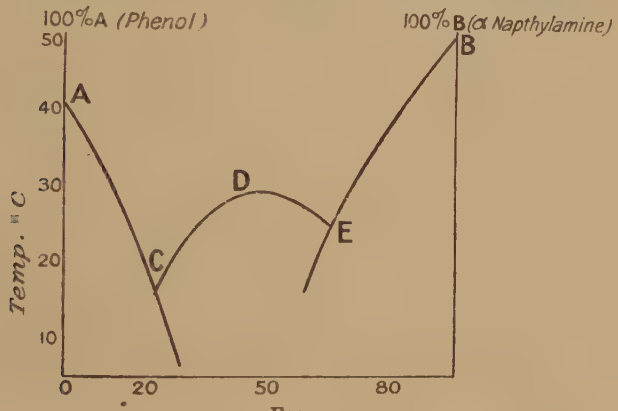


FIG. 43.

The solids present at the eutectic at C are phenol and C_6H_5OH, $C_{10}H_7NH_2$. The solids present at the eutectic at E are the same compound and the amine. The concavity of the curve CDE with regard to the concentration axis, the curve ending in two eutectics, is very characteristic of the presence of a compound. The same behaviour is shown by several alloys, *e.g.* magnesium and tin, the compound Mg_2Sn being produced, *cf.* Desch's *Metallography*. (The solution or liquid in contact with the pure solid at D may be regarded simply as the *molten* solid itself.) This is a good illustration of how purely physical methods can be employed to detect chemical combination. As we observe, there is a good theoretical reason for considering that a concave curve *of the above type* may be taken as evidence of the formation of a compound between the components. A convex curve showing a minimum melting-point, on the other hand (as in the system HgI_2, $HgBr_2$), does not mean the formation of a compound, though it does indicate the formation of a homogeneous eutectic. If the minimum point had really

been a point of intersection of two *separate* lines (a freezing-point line and a solubility line, as in the H_2O—NaCl case) we should be justified in considering the system at this point as a *heterogeneous eutectic.*

Liquid Mixtures.

So far some instances have been given of the behaviour of different sorts of two-component systems as manifested by the phenomena of freezing point and solubility. One or two instances of the behaviour exhibited by two-component systems in the change from the liquid to the vapour state may be briefly indicated. The most interesting problem is that of the distillation of mixtures. When the two components are quite immiscible the total vapour pressure = the sum of the pressures of the two substances (measured separately). In the process of distillation they are quite without influence on each other. When two liquids are partially miscible a distillate of definite composition at a constant temperature is obtained as long as the two layers are present in the distillation flask. When one layer only remains in the flask, and distillation is continued, the distillation proceeds as in the case to be considered next, namely, that of two liquids completely miscible in all proportions.

The behaviour of systems of this type varies according to the chemical nature of the components. The presence of each constituent lowers mutually the vapour pressure of each (*i.e.* the usual effect of the presence of a "solute" upon a "solvent"), and the boiling point may be higher or lower than the boiling point of either component, depending on the value of the sum of the vapour pressures, for under ordinary conditions boiling sets in when the sum of the vapour pressures = 1 atmosphere. In general the composition of the vapour, and therefore of the distillate which is simply condensed vapour, differs from that of the original mixture. In a simple case such as that of methyl alcohol and water, the water being in considerable excess, the vapour is much richer in the alcohol than is the liquid, and finally by distillation pure water is left in the retort. In certain cases we meet with the remarkable phenomenon known as *Mixtures of constant boiling point*, which can be distilled at constant temperature unchanged, *i.e.* the composition of the vapour or distillate remains unchanged. Such a mixture behaves as a single pure substance, and was indeed for long regarded as a *compound* of the two components, until it was shown by Roscoe that by altering the boiling temperatures (by altering the external pressure) a series of constant boiling mixtures could again be obtained, each of which differed, however, from one another in composition. A true compound, of course, could not alter in composition by simply altering the pressure. A constant boiling mixture is one which possesses either a *greater* vapour pressure than that of any other mixture of the two components, or possesses a *smaller* vapour pressure than that of any other mixture. Thus 96 per cent. ethyl alcohol + 4 per cent. water possesses a lower vapour pressure, and therefore

a higher boiling point, than that of any other mixture of these two components. If we start therefore with any smaller percentage of alcohol than this, and gradually raise the temperature distillation will occur in such a way that the distilling liquid loses water more quickly than alcohol, *i.e.* the distillate is richer in water than the original mixture until the composition of the liquid in the distilling flask reaches the value 96 per cent. alcohol, after which the remainder distils without change of temperature or composition. Similarly, if we started with a mixture of 98 per cent. alcohol, the process of distillation would have caused excess alcohol (along with some water) to pass over, the boiling-point rising until the constant boiling mixture was again reached. The mixture consisting of 70 per cent. propyl alcohol and 30 per cent. water happens to possess a higher vapour pressure than any other mixture of the two, so that if we start distilling a mixture of any other composition the distillate which comes over first, *i.e.* that which possesses the lowest boiling point, contains 70 per cent. propyl alcohol. This distils at a constant temperature until one or other of the constituents entirely disappears from the distilling flask. In this case it is possible to effect a complete isolation of one liquid in a single operation, which was impossible in the case of ethyl alcohol and water mixtures. The system hydrochloric acid and water is a well-known instance of such constant boiling mixtures, that containing 20·2 per cent. of acid having a minimum vapour pressure and boiling at 110° C. under atmospheric pressure. This behaviour is analogous to the ethyl alcohol—water system. The properties of liquid mixtures are, however, so varied, and of so specific a nature, that there is no opportunity to do justice to this subject in a general text-book. The reader is therefore referred to Sidney Young's *Stoichiometry*, in this series, and likewise to the same author's book, *Distillation;* also Kuenen's *Verdampfung und Verflüssigung der Gemischen* (in Bredig's Handbooks of Applied Physical Chemistry).

Liquid Crystals.

In dealing with transformation from one state to another, an important case still remains to be considered although its theoretical significance has not yet been generally agreed upon. The phenomenon referred to is the formation of so-called *Liquid Crystals.* As early as 1888 it was observed by Reinitzer that in the case of two solid substances, cholesteryl acetate and cholesteryl benzoate, each possesses the property of melting sharply at definite temperatures, but the liquid instead of being transparent is turbid and milky. This turbid liquid has a definite temperature range of stability, for on heating still further, the system becomes quite transparent at a given definite temperature. The same phenomenon is exhibited by a few other substances, notably by para-azoxyanisole and para-azoxyphenetole. The phenomenon is a reversible one in the chemical sense, *i.e.* on cooling the transparent liquid it assumes the turbid state at a given temperature and this in

turn solidifies to the solid, also at a given temperature. The turbid system is liquid in the sense that it flows like a liquid and can be made to assume the spherical form when placed in a liquid of the same density. It also exhibits the property of double refraction which is characteristic of certain crystals. Hence Lehmann (who has specially devoted himself to work in this field) coined the name "liquid" crystals. Discussion has centred round the problem: Is the turbid state heterogeneous or homogeneous? *i.e.* is it one phase or more than one? Its appearance is very similar to that of an emulsion, and this suggests heterogeneity. On the other hand it has not been possible to effect a separation of one phase from the other, and further, the existence of a sharp solidifying point and a sharp clearing point are evidence for homogeneity. A definite conclusion has not yet been reached.

The Two-Component System: Sodium Sulphate—Water.

At ordinary temperatures the solid which crystallises from a saturated aqueous solution of sodium sulphate is the deka-hydrate $Na_2SO_4 . 10H_2O$. At a temperature of 50° C. the solid which separates out is the anhydrous salt Na_2SO_4. It is clear that there must be a *transition temperature* at which both deka-hydrate and anhydrous salt may crystallise out together, since both are in equilibrium at the transition point. Solubility measurements have indicated this point very clearly. The results obtained are shown in the diagram (Fig. 44). From 0° C. up to the temperature 32·4° C. the deka-hydrate is the stable form, its solubility being indicated by the ascending line. From 32·4° C. onwards the anhydrous salt crystallises, and this salt shows the phenomenon of *retrograde solubility*, *i.e.* the solubility diminishes as the temperature rises. The point E (32·4° C.) is the transition point. This is a good instance of how solubility measurements can be utilised to indicate such regions of stability. In addition to the anhydrous salt and the deka-hydrate, another solid can, however, be prepared under certain conditions, namely, the hepta-hydrate $Na_2SO_4 . 7H_2O$. If a solution of sodium sulphate, saturated at the temperature 34° approximately, be cooled down in the absence of dust particles or other nuclei, it is possible to reach the temperature 17° C., when the solid which crystallises out will be found to be the hepta-hydrate. Determinations of the composition of the solutions in equilibrium with this hydrate at different temperatures from the region 0° C. allow us to plot the dotted line ascending to D. The solubility curve of the hepta-hydrate also shows a sharp change in direction at D, the solubility being now less as

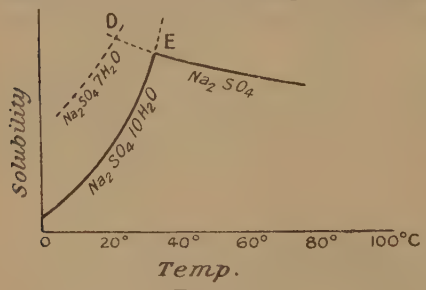


Fig. 44.

the temperature increases, and the solid phase separating out being the anhydrous salt. This is indicated by the dotted line DE, which continues past E on without a break. The point D corresponds to temperature 24·4° C., P = 18·9 mm., and is the transition temperature of the hepta-hydrate into the anhydrous salt. At D two solid phases (the anhydrous salt and hepta-hydrate) are in equilibrium with saturated solution and vapour. Since there are four phases, and the system is a two-component one, we must have $f = 0$, *i.e.* the system is invariant, and must be represented by a *point* on the diagram. On altering one of the variables, say, temperature, one of the phases must disappear. The phase which disappears is the hepta-hydrate, and we find the system travelling along the line DE. The transition point D and the lines leading to it are dotted, indicating meta-stability. This is clear, for the solubility of the hepta-hydrate is greater than the deka-hydrate at any temperature, and hence the hepta-hydrate must be unstable with respect to the deka-hydrate. Sodium sulphate forms therefore only one *stable* hydrate. The anhydrous salt is for the same reason unstable with respect to the deka-hydrate at all points from D to E. At temperatures higher than E, however, the solubility of the deka-hydrate would be greater than that of the anhydrous salt, *i.e.* from E onwards the anhydrous salt is the stable phase. It is important to notice that although we speak of the temperature 32·4° C. (point E) as the transition point from deka-hydrate to anhydrous salt, this limitation to the stability has reference to the solid form, not to the solutions. At all temperatures (say from 0° to 50°) the aqueous solution contains in all probability mixtures of anhydrous molecules and deka-hydrate molecules, there being an equilibrium between them as indicated by the equation—

$$Na_2SO_4 + 10H_2O \rightleftarrows Na_2SO_4 . 10H_2O.$$

This is a homogeneous equilibrium governed by the mass-action principle. The equilibrium varies with the temperature, but there is no reason for believing that in the *solution* below 32·4°, dekahydrate molecules *alone exist*, and above 32·4° anhydrous molecules alone exist. Both coexist over the temperature range. What must happen is, that as the temperature rises (say, we start below 32·4°) the homogeneous equilibrium shifts over to the left so, that just at 32·4° the solution is saturated with respect to anhydrous salt as well as with respect to deka-hydrate. On raising the temperature by an infinitesimal amount the equation likewise shifts more towards the left, the anhydrous salt being now super-saturated. Anhydrous salt crystallises (assuming retardation is prevented) and at the same time, by the principle of mass action, the equilibrium tends to maintain itself, that is some more anhydrous salt molecules are formed in the solution at the expense of the dekahydrate molecules, these being in turn supplied by the solid dekahydrate. The solid dekahydrate therefore begins to dissolve, *i.e.* disappear, just above E. The solution is, however, again super-saturated with respect to anhydrous salt, and this further precipitates itself, the above process

being repeated until *all* the solid dekahydrate has disappeared and we are left with the invariant system anhydrous salt solid—saturated solution—vapour. The discovery of the points E and D, and the solubility lines leading to and from them, exhaust by no means our information respecting the behaviour of this two-component system. The temperature-concentration and vapour pressure-temperature diagrams have recently been extended by A. Smits and J. P. Wuite (*Proc. Roy. Soc. Amsterdam*, **12**, 244, 1909-1910). The complete behaviour of the

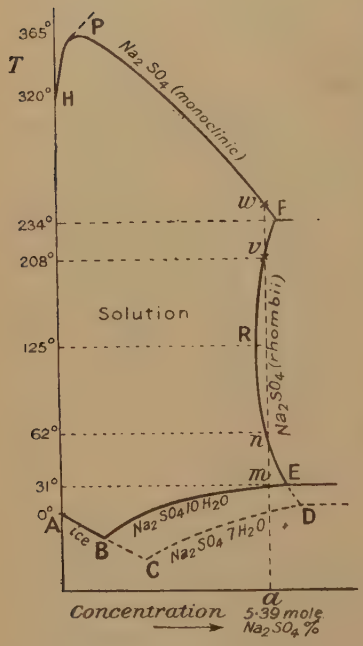


FIG. 45.

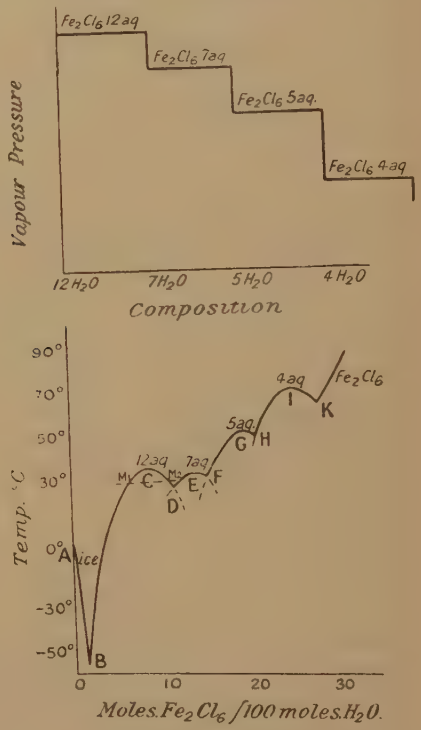


FIG. 46.

system as far as it can be shown on a temperature-concentration diagram, is illustrated by the accompanying figure (Fig. 45), in which temperature is denoted by the ordinates and composition (per cent. sodium sulphate) by the abscissæ.

If we commence with pure water at the point A (temperature 0°) and add sodium sulphate, we can trace out the line AB, which gives the temperatures at which ice is in equilibrium with (dilute) solutions of the salt. At B there is a eutectic point, the solids in equilibrium being ice and $Na_2SO_4 . 10H_2O$. If the system be super-cooled, no dekahydrate being allowed to form at B, we can reach the point C at

which there is another eutectic (a meta-stable one), the solids in meta-stable equilibrium being ice and $Na_2SO_4 . 7H_2O$. Returning to the point B and raising the temperature slightly, the ice will disappear, and the solid phase will consist of dekahydrate. By measurements of the solubility of the dekahydrate at various temperatures we pass along the line BE. (The same procedure at C would have taken us along CD, the solid being the heptahydrate.) At E, a new solid makes its appearance, *viz.* anhydrous rhombic Na_2SO_4. E is therefore another eutectic (32·4° C. and 30·8 mm. Hg), the solids in equilibrium being $Na_2SO_4 . 10H_2O$ and Na_2SO_4 rhombic. On raising the temperature the dekahydrate disappears and we follow the line ERF, which gives the solubility of rhombic Na_2SO_4 as a function of temperature. Starting from the meta-stable eutectic point D 24·4° C., we can similarly follow the line DERF. It will be observed that the solubility of Na_2SO_4 rhombic at first decreases with rising temperature, and eventually increases, the minimum being about 125° C. Theoretical reasoning on the significance of this retrograde curve is given by Smits, *l.c.*, **12**, 227, 1909-1910. When F is reached a sharp change in direction is experienced by the solubility curve, this being due to the appearance of a new solid phase which analysis shows to be Na_2SO_4 monoclinic. F is therefore a eutectic point (234° C. 27·5 atmospheres) discovered by Nacken.[1] On passing this temperature the monoclinic is the stable form the solubility of which decreases as the temperature rises. Finally we reach the point P, the temperature of which is 365° C. This is the critical temperature, the liquid being identical with the vapour. Since this temperature is practically the critical temperature of water itself, it is to be concluded that the solubility of the salt in the critical vapour is practically zero. The point P in fact lies quite close to the temperature T axis. (For the sake of clearness, the critical point has been drawn at too great a concentration, because otherwise one could not show that in P (the solubility melting point) the line passes continuously into the vapour line PH, which has been assumed as coinciding with the axis for H_2O below 320° C.)

The Two-Component System Ferric Chloride—Water.

This system is of interest, as it was the first case of systematic examination of the hydrated salts from the standpoint of the Phase Rule, undertaken by Bakhuis Roozeboom. The diagram (Fig. 46), in which the ordinates represent temperature and the abscissæ molar concentration of ferric chloride (reckoned as Fe_2Cl_6) per 100 moles of water, will illustrate the behaviour of this system. It will be seen that the following compounds are marked: $Fe_2Cl_6 12H_2O$, $Fe_2Cl_6 7H_2O$, $Fe_2Cl_6 5H_2O$, $Fe_2Cl_6 4H_2O$, Fe_2Cl_6 anhydrous. The discovery of these various compounds has been made possible by the application of the Phase Rule. In fact, the usefulness of the Phase Rule appears in many cases in which it is quite impossible to isolate a given compound, yet the

[1] Nacken, Smits and Wuite, *l.c.*

behaviour of the system indicates without doubt that such a compound exists. Let us begin by considering pure water (freezing point 0° C., point A, lower half of diagram) to which we add increasing quantities anhydrous ferric chloride. Measuring successive freezing points we pass along the line AB. At the point B the system will go completely solid, and microscopic analysis shows that there is a heterogeneous eutectic mixture formed at B, the phases being—solid ice, solid $Fe_2Cl_6 12H_2O$—solution—vapour. By raising the temperature and adding more ferric chloride we obtain the solubility curve BC, which passes through a maximum, and again another eutectic mixture is formed at D. From the shape of the curve BCD, one showing a maximum falling to a eutectic on each side, we infer the existence of a compound represented by the point C. This point corresponds to the formula $Fe_2Cl_6 12H_2O$. The solution has this composition, that is, the solution is really the fused solid. In other words, if we choose a solution having the composition indicated by C and slightly lower the temperature, it will be found that the whole system will solidify sharply at C, without change in temperature, thereby indicating the existence of a true compound, a conclusion which is supported by taking the shape of the curve into consideration. By the successive addition of salt and raising or lowering the temperature we can trace out the remainder of the diagram, which shows further eutectics at the points F, H, K, and also indicates the compounds at the points E, G, I. If a horizontal line be drawn just below C, as indicated in the figure, it will be seen that the solid dodecahydrate can exist in equilibrium at one and the same temperature, with two solutions of quite different concentrations indicated respectively by m_1 and m_2. The possibility of this from the kinetic standpoint is that the *sort* of molecules present in the two cases is different, or rather the relative proportions of certain sorts of molecules are different. As we have seen in dealing with the case of solutions of sodium sulphate we must consider that molecules of *all* the compounds are present, though at low temperatures and concentrations, say in the region of m_1, there will be exceedingly few of the anhydrous Fe_2Cl_6 molecules or of the tetrahydrate or pentahydrate, more of the heptahydrate, and a great many dodecahydrate molecules. In the concentration region m_2, there will be less dodecahydrate and a greater number of heptahydrate molecules. The equilibrium between all these different sorts of molecules in the homogeneous solution is presumably governed by the law of mass action. Owing to the continuous change in the molecular nature of the solution with rising concentration and temperature, we must not regard the solution m_2 as *simply* a more concentrated form of m_1, for if we did we would get the thermodynamically impossible case of one and the same substance (solid dodecahydrate) existing in equilibrium with the *same* solution at different concentrations.

If now we wish to isolate or prepare a given hydrate of ferric chloride all we have to do is to examine the diagram and note the concentration of solution and the temperature at which a pure hydrate solidifies, *i.e.* any of the points C, E, G, I. As a practical guide,

especially in technical practice such as in chemical manufacture, the Phase Rule is of great assistance.

The system ferric chloride—water may be used to illustrate an important point, namely, *the process of dehydration of a solid hydrate*. Each solid hydrate has a certain pressure of water vapour with which it is in equilibrium. The upper half of the figure shows diagrammatically the values of such pressures, called dissociation pressures, as a function of composition, the temperature being constant. Consider what happens if water be removed, by isothermal distillation or desiccation, from a hydrate of high water content (say the dodecahydrate). The diagram shows that the pressure will not alter continuously as distillation proceeds, but will alter discontinuously, remaining constant for a time, at a series of different values corresponding to the *dissociation pressures* of successive hydrates.

It is very important to note that "the dissociation pressure of a hydrate" is really the equilibrium pressure over *two* salts simultaneously. The vapour consists of water molecules, since those of the salt are practically non-volatile. *The "dissociation pressure of a given hydrate" (say the dodecahydrate) might be regarded as identical with the "true" vapour pressure of the next lower hydrate (the heptahydrate)*, as far as affinity processes are concerned, *cf.* Chap. XII. The dodecahydrate exists in equilibrium with solid heptahydrate and water vapour at the dissociation pressure of the dodecahydrate. (Naturally the producion of water molecules from the salt must have dehydrated a small portion of it at least to the next lower hydrate.) We have thus a two-component system existing in three phases, and as we have assumed the temperature constant, it follows that the pressure must be fixed, namely, the dissociation pressure. On continuing the desiccating process, solid heptahydrate is produced at the expense of the dodecahydrate at constant temperature and pressure, until finally the last trace of dodecahydrate disappears, the pressure being still the same, and the solid being the heptahydrate. Such a state of things, however, is only a limiting case, for if the smallest quantity of water is further removed some pentahydrate is formed, and the pressure falls suddenly to the "dissociation pressure" of heptahydrate. The same change is observed when the hepta-body entirely disappears and the solid system consists of penta- and tetrahydrate, a further change being observed when the pentahydrate disappears and the tetrahydrate is partly converted into anhydrous salt. The water vapour, which is at the dissociation pressure of tetrahydrate, is in equilibrium with tetrahydrate and anhydrous salt simultaneously. If we continue removing water vapour all the tetrahydrate may be made to vanish at constant temperature and pressure, and we find in the limit that the anhydrous salt can exist in equilibrium with a certain pressure of water vapour, namely, "the dissociation pressure of the tetrahydrate". The distinction between "true" vapour pressures over a solid and the dissociation pressure will be clear when we come to study affinity of hydrate formation.

We have seen that in the case of a hydrated salt we cannot properly

use the term vapour pressure except in the sense of dissociation pressure, *i.e.* two solids must be present simultaneously to give a definite pressure at a given temperature. We are only considering, of course, the vapour which consists of H_2O molecules. The principle of work has been used as a criterion of equilibrium in the case of changes which involve no volume alteration, the criterion being that $(\delta A)_{vT} = 0$, (*cf.* Chap. IV.). It might be concluded from this that the vapour pressure over a saturated solution of a given hydrated salt is the same as that over the solid salt itself—the vapour in both cases consisting of H_2O molecules. This conclusion is incorrect, however, for the single salt in contact with vapour is unstable, the stable system consisting of two salts and the vapour. Over a certain temperature range a solution may be kept saturated with respect to a single salt, say, $MgCl_26H_2O$, whilst the vapour pressure measured in the case of the solid material is really the dissociation pressure due to two substances, $MgCl_26H_2O$ and $MgCl_24H_2O$ present simultaneously. It is only at the transition point that we can regard the hexahydrate as "equivalent" to the tetrahydrate, and hence it is only *at the transition temperature* that the *vapour pressure over the saturated solution* of the hexahydrate *or* of the tetrahydrate *is the same as the dissociation pressure* over the two solid salts. This point may be illustrated by the following data selected from those obtained by Derby and Yugve (*Journ. Amer. Chem. Soc.*, **38**, 1439, (1916)), in the case of the hexahydrate and dihydrate of cobalt chloride.

Temperature, °C.	Vapour Pressure over the Saturated Solution of $CoCl_26H_2O$.	Dissociation Pressure of the Hexahydrate and Dihydrate, Solid Salts.
20	11·8 mm.	5·4 mm.
30	19·7 ,,	10·2 ,,
40	31·3 ,,	21·2 ,,
50	45·9 ,,	41·9 ,,
52·25 (transition temperature)	48·6 ,,	48·6 ,,

As a further illustration of the same principle we may take the data obtained by Derby and Yugve in the case of the hexahydrate and tetrahydrate of magnesium chloride (see opposite page).

It will be observed that at the transition temperature the vapour pressures are identical. In the above case we meet with the peculiarity that the vapour pressure over the saturated solution actually decreases in the neighbourhood of the transition temperature, *i.e.* the vapour pressure curve becomes retroflex. This is due to a large increase in solubility of the hexahydrate near its transition temperature, a great solubility necessarily depressing the vapour pressure. Naturally, no such effect is observed in the case of the solid salts.

The study of three and more component systems would take us

beyond the scope of this book. The reader is therefore referred to the special works and papers already mentioned. This chapter will be concluded with a brief description of Smit's new theory of allotropy, which is of fundamental importance.

Temperature, ° C.	Vapour Pressure over the Saturated Solution of $MgCl_2 6H_2O$.	Dissociation Pressure of the Hexahydrate and Tetrahydrate, solid Salts.
30	10·1 mm.	1·5 mm.
40	17·3 ,,	2·5 ,,
60	43·8 ,,	8·3 ,,
80	93·4 ,,	26·2 ,,
100	166·5 ,,	75·0 ,,
110	197·7 ,,	127·5 ,,
115	194·0 ,,	160·0 ,,
117·2 (transition temperature)	169·1 ,,	169·1 ,,

The Phenomenon of Allotropy.

Owing to the amount of research which has been devoted to this subject during recent years it is necessary to survey briefly some of its more important features.

When one and the same *compound* can exist in two or more forms (differing in crystalline form and other physical properties) the compound is said to exhibit isomerism or polymorphism. In the case of some elements, such as sulphur, phosphorus, selenium, and tellurium, a similar phenomenon has been observed, to which the name *allotropy* has been given. There are now three types of allotropy recognised. First, the allotropy may be *Enantiotropic*, the different varieties of an element possessing definite temperature ranges of stability and convertible one into the other at a certain temperature and pressure called the transition point. An example is the grey and white tin transformation (Cohen, *l.c.*) which has already been referred to. Secondly, the allotropy may be *Monotropic*, that is, one variety is perfectly unstable at all temperatures and pressures. The unstable form tends to pass continuously into the stable. An example of this is explosive antimony, investigated by Cohen and his collaborators. Thirdly, we have *Dynamic allotropy*. In this case the different varieties or allotropes can exist together in certain proportions, there being an equilibrium between them (presumably governed by the law of mass action), such equilibrium points being shifted by change in temperature. The phenomenon of dynamic allotropy is quite analogous to that of dynamic isomerism, except that in the first the substance is an element, in the second the substance is a compound.

The first case of dynamic allotropy, namely, that of liquid sulphur, was investigated by Alexander Smith and his collaborators (*Journ. Amer.*

Chem. Soc., 1903, and onwards), who showed that liquid sulphur is a mixture of a light mobile variety soluble in carbon bisulphide and denoted by the symbol S_λ, together with a dark viscous variety insoluble in carbon bisulphide denoted by S_μ. Ordinary liquid sulphur at the "natural freezing point," 114·5° C., consists of 3·6 per cent. S_μ, the remainder being S_λ. The freezing point is, however, characterised by the phenomenon of variability according to the composition of the liquid, *i.e.* according to the amount of S_μ present, and according to the solid phase separating out. The following data are given by Smith and Carson (*Zeitsch. physik. Chem.*, **77**, 661, 1911) for the "ideal freezing points" when no S_μ is present and the "natural freezing points" when the S_μ is present in the liquid in the equilibrium proportion.

	Ideal F.P.	Natural F.P.
Prismatic (Monoclinic) Sulphur (S_1) .	119·25°	114·5° (3·6% S_μ)
Rhombic Sulphur (S_2)	112·8°	110·2° (3·4% S_μ)
Nacreous Sulphur[1] (S_3)	106·8°	103·4° (3·1% S_μ)

In the light of these facts regarding the complex nature of this apparently simple system, we must receive with caution the numerical values of the melting points already given in our earlier discussion of this system. The earlier discussion served to bring out the general principles involved, but with regard to measurements under high pressure especially, the earlier data cannot be accepted as quantitatively correct. Smith has found that the transformation into amorphous sulphur is accompanied by a diminution in volume, and therefore the tendency to produce amorphous sulphur must be greater the greater the pressure. The earlier data quoted in Fig. 38 were obtained prior to Smith's discovery that sulphur dioxide and other acids prevented the formation of amorphous sulphur, whilst ammonia made the formation very rapid. The results graphed in Fig. 38 neither represent true equilibrium conditions nor do they represent sulphur free from amorphous sulphur.[2]

The phenomenon of allotropy has recently been investigated and the theoretical views extended by Smits and his co-workers (A. Smits, *Zeitsch. physik. Chem.*, **76**, 421, 1911; *ibid.*, **77**, 367, 1911; also *Proc. Roy. Soc. Amsterdam*, **12**, 763, 1909-1910; *ibid.*, **13**, 822, 1911; *ibid.*, **14**, 1199, 1912). Smits emphasises the idea that not only does the *liquid*, *i.e.* the fused element, contain molecules of different sorts, but that the solid separating is likewise a solid solution, the inner equilibrium existing in the liquid state having its counterpart in the solid state as well. Following out this idea, Smits has shown the relation which exists between the three kinds of allotropy, for a consideration of

[1] This variety may be prepared in needle-shaped crystals by heating sulphur to 150° C., cooling to 98° C., and making it crystallise by scratching.

[2] Private communication from Professor Alexander Smith.

which the reader is referred to the original papers. Before considering the case of phosphorus, which we shall take as an illustration of Smits' method of treatment, it is necessary to consider the means whereby the existence of inner equilibrium between different sorts of molecules can be inferred.

NOTE.—A unary substance is one whose molecules are all identical physically as well as chemically. A pseudo-binary substance is one whose molecules are chemically the same (as regards ultimate analysis), but nevertheless may be divided into two sorts differing from one another in respect of "physical" properties, and there exists an equilibrium between the two sorts.

The Significance of Melting-point Determinations from the Standpoint of the Theory of Allotropy.

Consider the diagram (Fig. 47), in which the ordinate denotes *temperature*, and the abscissæ *time*. In the case of an absolutely unary body consisting of molecules of only one sort, both in the liquid and solid states, the curve obtained would be similar to that shown with a perfectly horizontal portion during the process of solidification. ABCD represents the cooling curve, *i.e.* the temperature-time curve, which we get when a substance behaves as a *perfectly unary substance*, and the heterogeneous equilibrium (*i.e.* transformation of phase at constant temperature) between the liquid substance surrounding the immersed thermometer and the outer solidifying layer (which is in contact with the cooling bath) sets in rapidly enough for the loss of heat to be compensated by the heat evolved by the process of crystallisation. The rounding at B is due to the fact that the thermal conductivity of the liquid is *not* perfect, and therefore thermal equilibrium between outer and inner parts cannot be established instantaneously. Solidification in the outer layers begins before the liquid in the immediate neighbourhood of the thermometer bulb has fallen to the temperature of solidification. The flat part BC is due to heat compensation. That is when the liquid round the thermometer has reached the temperature of solidification, the heat lost to the bath is balanced by heat evolved on crystallisation, and the horizontal part of the curve results. Before the mass has, however, become entirely solid, a change sets in, because the thermometer comes more and more in contact with the solid substance, which in so far as the bulb is not in direct contact with the liquid will possess a lower temperature than the liquid, and will produce in its readings the rounding at C, until the last trace of liquid has vanished. If the *heterogeneous equilibrium*, *i.e.* the transformation of solid into liquid at constant temperature, is not established with very great rapidity,

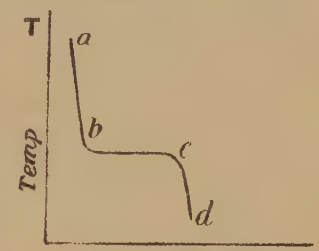


FIG. 47.

the loss of heat can no longer be compensated by the heat of crystallisation, in consequence of which the liquid in contact with the solid is super-cooled. In this case a more or less *descending* line will be found instead of the horizontal part. Besides this lag or hysteresis in the *heterogeneous* equilibrium solid $\rightleftarrows$ liquid causing a sloping freezing curve, it is also conceivable that the super-cooling might be attributed to the fact that the *homogeneous* inner equilibrium between different sorts of molecules of the same compound, has not set in quickly enough, *i.e.* the substance is not acting as a unary one. Accordingly, to decide by means of cooling curves whether or no a substance behaves in a unary way, we must pursue the following course: *during the actual cooling curve the circumstances are made as similar as possible* (*in a series of experiments*) *whereas the previous history of the* (*liquid*) *substance is made as different as possible*, *i.e.* it is raised to different temperature stages, and quickly brought down to the freezing point, the idea being that the inner equilibrium will thus vary from case to case, and will manifest itself by different forms of solidifying curves, the heterogeneous equilibrium changes being presumably kept the same in successive experiments by freezing at the *same rate*, etc. In the actual case the liquid substance is first allowed to super-cool a little, and is then "seeded" in some way, because the maximum to which the temperature then rises in the subsequent solidification can give valuable information regarding the existence or non-existence of inner equilibrium, *i.e.* as regards settling whether a substance is unary or not. Smits has examined in this way the systems: *Mercury* (which behaved as a unary substance, and may therefore be regarded as composed of identical molecules); *tin* (which proved to be complex, possibly pseudo-binary, *i.e.* two sorts of molecules); *water* (which also proved to be complex, the "freezing point" varying from $-0{\cdot}28$ to $-0{\cdot}06$ when solid ice was rapidly heated); and finally *sulphur* and *phosphorus*, the latter of which will be now considered briefly.

Phosphorus probably exists in three solid forms as well as liquid and gaseous (Jolibois, *Comptes Rendus*, **149**, 287, 1909; **151**, 382, 1910)—white phosphorus, red, and pyromorphic or violet phosphorus. After considerable trouble perfectly *pure* white phosphorus was obtained, *i.e.* white phosphorus which on being heated slowly gave a sharp melting point. It was found to be 44·0° C. Having thus an apparent unary behaviour as far as *slow* temperature changes are concerned, the next thing was to see if, by rapid heating or cooling, the real inner complexity would manifest itself. The following is a description of three experiments. The melting point vessel was first placed in boiling water for some time and then suddenly transferred to a bath at 15° C. to make the cooling take place so rapidly that the internal equilibrium could not keep pace with it. When the grafting[1] took place at about 43·5° C., after taking out of the bath, the temperature rose above 44° C., from which it followed, that when the cooling takes place very

[1] The grafting was effected by breaking off the capillary ending to the tube and inserting it for a moment in solid CO_2. Solid phosphorus was thereby formed.

rapidly the liquid phosphorus is already super-cooled at 44° (its true *unary* melting point). In a second case the grafting took place *above* 44° C. and the temperature rose to 45·5°, and Smits succeeded in getting a rise to 46° with grafting at a still earlier stage. In the experiment corresponding to the curve given (Fig. 48) grafting took place at about 44·5° C.; at first the temperature descended, then rose to 45·05°, after which it fell again, at first pretty rapidly, then less rapidly, and at last very rapidly again. The whole line shows the type of a line of solidification of a *mixture*, the melting range being here about 1·8°, but it can be considerably larger still. When solid phosphorus, even when rapidly cooled so as to exhibit the phenomena just described, is allowed to stand for a short time inner equilibrium rapidly sets in. The second

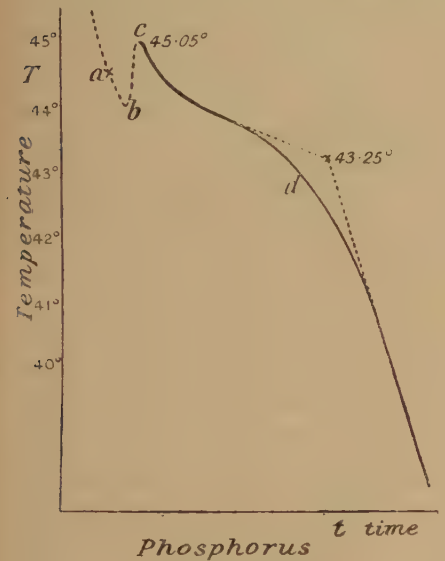


Fig. 48.

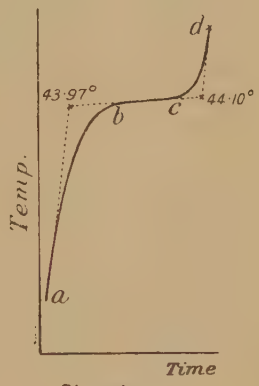


Fig. 49.

curve (Fig. 49) is a heating curve which shows what was observed after the solid substance obtained in the previous experiment was suddenly placed in a bath at 50° C. The heating curve shows that after some minutes a considerable approach to the state of internal equilibrium has taken place but has not been reached as yet, for the melting range still amounts to 0·13° C. and the end melting point lies above the unary melting point. Now Smits assumes that phosphorus really possesses *two* kinds of molecules mutually convertible. He denotes these hypothetical "forms" of phosphorus by P_α and P_β. The actual forms we meet with (white, red, and violet) are really solid solutions of P_α and P_β, and differ from one another in their percentage composition in respect of these constituents. Of course it could scarcely be hoped to

ever realise experimentally pure 100 per cent. P_α or 100 per cent. P_β, because of the rapid change each of these would undergo into some known form where α and β molecules are both present. Smits takes P_α to be "probably colourless". This seems to be necessary because Chapman (*Trans. Chem. Soc.*, **75**, 743, 1899) found that red phosphorus melts to a colourless liquid and in becoming liquid there must have been a shift towards one or other of the hypothetical forms—we may take this one to be P_α. The behaviour of the system phosphorus, so far as it is known to us, could according to Smits be accounted for if we take the various phases known to be related to one another in terms of α and β (as regards their constitution and range of stability), as given in the accompanying diagram (Fig. 50). The line kl_2l_1 denotes the internal equilibrium in the liquid at different temperatures, and s_1n refers to the internal equilibrium (over a small temperature range) in *solid white phosphorus*, so that s_1 and l_1 indicate the solid and the liquid phases which are in internal equilibrium and coexist at the unary melting point of white phosphorus (44° C.). Now it follows from the course of the lines that if the liquid l_0 is cooled very rapidly, the system will move down the dotted vertical line and crystallisation will occur already at l'_1 (the composition of the solid being s'_1). Then, in the *absence* of internal transformation, a melting range l'_1l_1 would be found, whereas in the case of rapid heating of the solid phase n the melting will already begin at s'_2 and be completed at s_1. Internal conversions, however, are not absent, so that "a transgression of the unary melting point is always much smaller than the lines l'_1l_1 and s'_2s_1 would lead us to expect". Further, the figure shows that the initial solidification will appear the sooner according as a higher temperature is started from, the system passing down (if cooled quickly) an imaginary vertical line from any point on the kl_2l_1 line. Similarly we see that initial melting

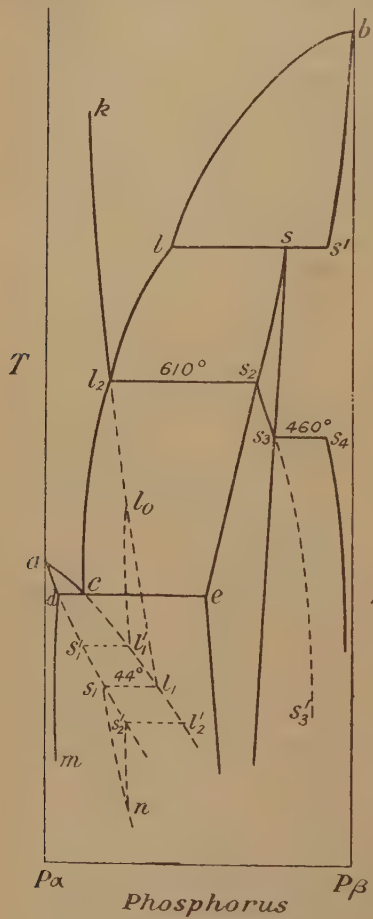


FIG. 50.

will appear the sooner (*i.e.* at a temperature lower than 44°) the lower the temperature we start from. All this is to be expected on the theory of allotropy, treating phosphorus as a pseudo-binary system. Jolibois has remarked that violet phosphorus is stable below 460° C. and above this temperature the red modification is stable, which melts to a colourless liquid at 610° C. Smits points out that a pseudo-binary system, *i.e.* a system consisting of two sorts of molecules, can be made to account for the existence of three actual crystalline modifications provided that it is assumed that there is a second discontinuity in the series of solid solutions. This has been done in the figure. The liquids along *bl* coexist with the solid solutions *bs'*, the liquids along *lc* coexisting in equilibrium with the solid solutions *se*. In this figure s_2 represents the unary melting point of *red* phosphorus, the liquid in equilibrium being represented by l_2 (temperature 610°). Below this temperature *red* phosphorus remains stable to 460° (*i.e.* the system cooled *slowly* will pass from s_2 to s_3). At 460° the red s_3 is converted into violet s_4, which is therefore stable below 460° C.

It must be remembered that a considerable part of the above equilibria at the present time are of a hypothetical nature only. Other views on the composition of the phosphorus system are held, for example, by Cohen and Olie (*Zeitsch. physik. Chem.*, 71, 1, 1910).

CHAPTER XI.

Chemical equilibrium in heterogeneous systems (from the thermodynamic standpoint) when capillary or electrical effects are of importance—Adsorption—Donnan's theory of membrane equilibria—Micelle theory of colloidal electrolytes.

Adsorption

The phenomena with which we have to deal are those which are manifested at the interface where two phases meet. The general treatment of the behaviour of heterogeneous systems in which surface or interface effects due to capillarity have to be taken into account (as for example the stability of colloidal solutions and emulsions), from the standpoint of a modified Phase Rule, has been left so far almost untouched. Within recent years Pawlow (*Zeitsch. physik. Chem.*, **75**, 48, 1910) seems to be the only investigator to have attempted this difficult problem, but, rather remarkably, his work has received little or no attention. Willard Gibbs himself pointed out in his original memoirs on "Equilibrium in Heterogeneous Systems" (*Scientific Papers*, Vol. II.) that in addition to the variables already considered in the Phase Rule, namely, temperature, pressure, and concentration, one must also take into account the surface area of the interface (or interfaces). The difficulty is to settle the correct number of equations connecting these variables.

Donnan has investigated the problem of stability of colloidal solutions from the thermodynamic standpoint, starting with the idea of an effective negative surface tension. His investigation, which is an extension of that given in Vol. I. of this book, will be found in the *Zeitsch. physik. Chem.*, **46**, 197, 1903.

Instead of pursuing so general a method of treatment, the subject of capillary chemical effects has been studied experimentally, by investigations of Gibbs' expression for the surface concentration effects due to surface tension. Gibbs (*loc. cit.*) showed as a thermodynamical necessity that IF A DISSOLVED SUBSTANCE HAD THE PROPERTY OF LOWERING THE SURFACE TENSION OF THE SOLUTION (SAY, AT THE LIQUID | AIR SURFACE), THE SUBSTANCE WOULD EXIST AT A HIGHER CONCENTRATION IN THE SURFACE LAYER THAN IN THE BULK OF THE SOLUTION.

This surface concentration is identified with the phenomenon of Adsorption, although it must be remembered that effects which are usually described under this title partake more frequently, in part at least, of partial solution of the substance in the second phase, and also possibly include some kind of purely chemical change, not taken account of by the simple physical theory. The property possessed by charcoal

of removing substances (such as colouring matter) from solution, or "absorbing" gases and vapours, is certainly an example of adsorption purely physical in the first place (and perhaps entirely), but possibly also partaking of the nature of solubility, such as that to which the Distribution Law applies. The process of dyeing is also an instance of physical adsorption, followed in many cases by chemical changes in the dye itself or even in a chemical reaction between the dye and the material dyed. The fastness of dyes, the greatest desideratum from the technical standpoint, means simply the irreversibility of the process, and this is in itself sufficient to show that dyeing cannot be entirely due to physical adsorption dealt with in the Gibbs' theory, since it is explicitly assumed in the latter that the surface concentration effects are reversible. Investigation of the Gibbs' expression must therefore be made under conditions where chemical effects and solubility of the solute in the adsorbing phase (the charcoal, for example) are reduced to a minimum. There can be no doubt that more complete information of this purely physical phenomenon is the first step towards a rational understanding of the more complicated phenomena of the dye-house and the filter bed.

Since the Gibbs' adsorption equation (as we shall call it) is thus of very considerable importance for capillary chemistry, the deduction of the equation by means of a thermodynamical cycle will not be without interest.

Deduction of the Adsorption Equation.

The following is the deduction given by Freundlich (*Kapillarchemie*, p. 50). (For an alternative proof, *cf.* Harlow and Willows, *Trans. Faraday Soc.*, **11**, p. 53, 1915. A more accurate expression is given by Porter, *ibid.* (p. 51).

Consider a dilute solution of volume v, osmotic pressure P, in contact with a vapour phase consisting only of the vapour of the solvent. The area of the separating surface between liquid and vapour is s, and the surface tension is σ. The solution is placed in a vessel fitted with a piston having a semi-permeable membrane, the solution being on one side of the membrane, and on the other side an infinite reservoir of pure solvent in contact with it. The following cyclic process is carried out.

The surface area is increased by the amount ds, the work done being $-\sigma ds$. The volume of the solution is considered as having remained constant. At the same time the osmotic pressure P may have altered—its new value being given by the expression $\left(\mathrm{P} + \frac{\partial \mathrm{P}}{\partial s} ds\right)$. The volume of the solution is now increased by dv, by pulling out the piston, the work being $+ \left(\mathrm{P} + \frac{\partial \mathrm{P}}{\partial s} \partial s\right) dv$. The surface area s is supposed to have remained constant in this last operation whilst the tension σ has changed to the value $\left(\sigma + \frac{\partial \sigma}{\partial v} dv\right)$. The surface area now contracts to

its initial value, the work gained being $+\left(\sigma + \frac{\partial\sigma}{\partial v}dv\right)ds$. P has now returned to its initial value, and when the piston is pushed in, thereby doing the work $-$ Pdv, the system has returned to its initial state. Since the process is isothermal and reversible the total work is zero. That is—

$$-\sigma ds + \left(\mathrm{P} + \frac{\partial \mathrm{P}}{\partial s}ds\right)dv + \left(\sigma + \frac{\partial\sigma}{\partial v}dv\right)ds - \mathrm{P}dv = 0,$$

or

$$\frac{\partial\sigma}{\partial v} = -\frac{\partial \mathrm{P}}{\partial s} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation states that if the surface tension alters with the volume, that is with the concentration, then the osmotic pressure must alter with the surface area. The latter can only be the case if the concentration of the solute in the bulk of the solution depends on the surface area, and this can only be so if the concentration in the surface layer is greater or less than that in the bulk of the solution.

From the above we see that the concentration c of the solution is a function of v (volume) and also of s (surface area). If n moles are dissolved, then we cannot simply write $c = \frac{n}{v}$, but instead we must allow for the fact that in the surface layer the solute is present to a greater or less extent than in the bulk. Suppose we denote this positive or negative excess in the surface layer by Γ, where Γ is mass of solute reckoned per unit area of surface. Then if the surface area is s, the quantity of solute in excess in the surface layer is Γs, and hence the actual concentration in the bulk of the solution is given by $c = \frac{n - \Gamma s}{v}$. Note that the quantity Γs may be positive or negative. We can now rewrite the above equation (1) in the form—

$$\frac{\partial\sigma}{\partial c} \cdot \frac{\partial c}{\partial v} = -\frac{\partial \mathrm{P}}{\partial c} \cdot \frac{\partial c}{\partial s} \quad . \quad . \quad . \quad . \quad (2)$$

But

$$\frac{\partial c}{\partial v} = \frac{-(n - \Gamma s)}{v^2}$$

and

$$\frac{\partial c}{\partial s} = -\frac{\Gamma}{v}$$

so that equation (2) becomes—

$$c\frac{\partial\sigma}{\partial c} = -\Gamma\frac{\partial \mathrm{P}}{\partial c}.$$

Since the solution is a dilute one we can apply the gas law $\mathrm{P} = \mathrm{RT}c$, so that we finally obtain—

$$\Gamma = -\frac{c}{\mathrm{RT}} \cdot \frac{\partial\sigma}{\partial c}.$$

This equation states that if the surface tension *decreases* as the concen-

tration of the solute *increases*, then Γ is positive, that is the concentration of the solute in the surface layer is *greater* than its concentration in the bulk. This is positive adsorption. On the other hand, if the surface tension increases as the concentration increases, there will be a negative adsorption or desorption of the solute in the surface layer. Finally, if the surface tension be independent of concentration, the concentration will be the same in both bulk and surface layer. The experimental investigation of this equation was first attempted by Donnan and W. C. McC. Lewis (*cf.* Lewis, *Phil. Mag.*, 1908; *ibid.*, 1909). Experiments were made with aqueous solutions of sodium glycocholate and also dyestuffs and other substances, notably caffeïne, which exerted by their presence considerable lowering upon the surface tension of the water. These substances likewise exerted a considerable lowering on the interfacial tension between a pure hydrocarbon oil and the aqueous solutions. It was shown that the substances did *not* dissolve in the oil and no chemical action was to be anticipated, so that the condit ons seemed favourable for the verification of the expression. The interfacial tension between the oil and aqueous solutions of various concentrations was measured, the tangent to the curve thus obtained at any given concentration (c) representing the value of $\frac{d\sigma}{dc}$. The right-hand side expression could thus be calculated. In the case of sodium glycocholate and the dyestuffs it came out to be of the order 10^{-7} gram/cm.^{2}. The value of the left-hand side was directly determined by two different methods. In the first method the oil was emulsified (*i.e.* broken up into fine droplets) by shaking with the aqueous solution, the change in concentration of the bulk of the solution being determined (the concentration-interfacial tension curve was itself used as the analytical means as it was the most delicate). Only a very small change in concentration was observed. By microscopic measurements, the size of the oil particles was determined and hence their number and hence the total adsorbing surface area. Knowing the total quantity of solute removed from the bulk of the solution, and the total absorbing surface, one obtains directly the mass adsorbed per cm.^{2}. The order of magnitude in the case of these substances was 10^{-6} gram/cm.^{2}. There is thus a large discrepancy between the "observed" value of Γ and the "calculated". Thinking that the great curvature of the emulsion particles might have something to do with this, a second method was employed, in which a stream of large oil drops was passed for a long time through the solution, the change in concentration being again determined. The results came out almost identical with those obtained by the first method. With the caffeïne, however, although the quantity adsorbed was much less than in the foregoing cases, approximate agreement was obtained, *viz.* the observed and calculated value of Γ was of the order 10^{-8} gram/cm.^{2}. It seems likely, therefore, that in the case of the dyestuffs and sodium glycocholate (which exhibit certain colloidal properties) the discrepancy is due to colloidal gelatinisation or flocculation on the oil surface, an

effect which is not taken account of in the simple physical relationship. The discrepancy is therefore no evidence against the validity of Gibbs' expression; the discrepancy is due to the colloidal nature of the solute examined. Later measurements by Lewis (*Zeitsch. physik. Chem.*, **73**, 129, 1910) on the adsorption of caffeïne by mercury (the caffeïne being dissolved in aqueous alcohol) showed agreement as regards order of magnitude. Besides the measurements at the interface of two liquids, Donnan and Barker (*Proc. Roy. Soc.*, **85** A., 557, 1911) have measured the adsorption of nonylic acid and saponine at the liquid | air surface. The air was passed in the form of bubbles through a column of the solution, diaphragms being inserted in the column so as to avoid general stirring of the liquid. As the bubbles passed up they carried with them a layer of higher concentration of the nonylic acid than that of the bulk, so that a decrease in concentration of the nonylic acid in the lower parts of the solution occurred. This was determined and likewise the total surface area of the adsorbing bubbles, and hence the value of Γ. In the case of very dilute solutions the adsorption was found to be of the order 1×10^{-7} gram/cm.^{2} for nonylic acid, and of the order 4×10^{-7} gram/cm.^{2} for saponine. The calculated values of Γ for nonylic acid, namely, the expression $-\frac{c}{RT}\frac{d\sigma}{dc}$, were of the order $(0{\cdot}26 - 0{\cdot}63)10^{-7}$ gram/cm.^{2}, the quantity adsorbed increasing with the bulk concentration of the solution. In the case of saponine, the calculated value of Γ was $(1{\cdot}36 - 1{\cdot}60) \times 10^{-7}$ gram/cm.^{2}. There is thus satisfactory agreement between observed and calculated values at least as far as order of magnitude is concerned.

A considerable difficulty enters if we have to try and allow for electrocapillary adsorption as well as pure adsorption, such as probably takes place in the case of mercury salts in aqueous solution in contact with a mercury surface, for there exists here a contact difference of potential which modifies the value of the interfacial tension even apart from concentration of the solute. We have here to take account of adsorption of ions as well as adsorption of molecules.[1] Practically nothing is known about such phenomena, though it is very evident that they play a *rôle*—and perhaps a fundamental *rôle*—in the mechanism of the processes involved in the precipitation of colloids by electrolytes.

The problem of simultaneous adsorption of solvent (water) and solute (inorganic salt) by an adsorbent (charcoal) has been investigated by A. M. Williams in Donnan's laboratory (*Trans. Faraday Soc.*, **10**, 155, 1914). As the concentration of the solute is altered, water displaces the salt, the adsorption of the salt being at first positive and later effectively negative, *i.e.* negative adsorption.

Solid Surface Films.

In the preceding section, the discrepancy between the observed adsorption and that calculated on the basis of Gibbs' equation has been ascribed to the formation of a gelatinous layer of the colloidal solute,

[1] An attempt in this direction has been made by the writer. (Compare Lewis, *Zeitsch. phys. Chem.*, 83, 129, 1910.)

If such a process occurs, the surface layer becomes heterogeneous (two-phase), and thus does not conform to one of the fundamental assumptions, *viz.* homogeneity in the surface layer and bulk of solution, made in deducing Gibbs' equation. The effect can be regarded as an excessive adsorption due in the first place to the lowering of the surface tension to a very marked extent, which results in the solubility of the solute being overstepped and consequent flocculation in the surface layer. Such effects have actually been observed by Ramsden (*Zeitsch. phys. Chem.*, 47, 336 (1904)) in the case of solutions of albumen, soap, saponine, and certain dyestuffs. All these substances have the property of lowering the surface tension of water. On shaking these solutions, foams are produced which possess considerable stability and rigidity, the rigidity being due to flocculation already referred to. It is possible, by shaking, to remove albumen in this manner from solution, the albumen collecting in the foam. Further, under these conditions the albumen is in the insoluble form, *i.e.* some change, chemical or physical, has been brought about as a result of the conditions which obtain in the surface layer. Ramsden has drawn attention to the close relations which exist between the formation of solid or semi-solid films, surface elasticity, and stability of foam. It has been shown also that if two such solutes are present, that which lowers the surface tension most markedly is the one which forms the surface aggregates. This behaviour is analogous to the preferential adsorption of solutes which remain in true solution, in the surface layer as well as in the bulk of the solution. It is, of course, unjustifiable to apply Gibbs' equation to those cases in which solid to semi-solid films are formed, even though capillarity is the primary cause of the increase in surface concentration which in turn leads to the formation of the film.

Donnan's Theory of "Membrane Equilibria".[1]

The problem dealt with is the distribution of ions on each side of a membrane, the ions being due to an "electrolytic colloid," like Congo red in water. Congo red is the sodium salt of an organic acid, the molecules and anions of which cannot pass through the membrane. This is of importance for the theory of dialysis and colloids, as well as for the mechanism of living plant and animal cells.

Consider a salt NaR dissolved in water, the solution being in contact with a membrane (denoted by a vertical line) which is impermeable to the anion R′ and also to the undissociated molecules NaR, but will allow $Na^{\cdot}$ and any other ions to pass through it freely. We suppose that on the other side of the membrane there is an aqueous solution NaCl. The initial state of things will be represented by

$Na^{\cdot}$	$Na^{\cdot}$
R′	Cl′
I.	II.

[1] *Zeitsch. f. Electrochemie*, 17, 572, 1911.

The NaCl will begin to diffuse from II. into I. until an equilibrium state is reached, represented by—

I.	II.
$Na^{\cdot}$	$Na^{\cdot}$
R'	
Cl'	Cl'

Now at the equilibrium, if a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged, *i.e.* no work will be done. The change here considered is the transfer of δn moles of $Na^{\cdot}$ and Cl' from II. to I. The work which we set equal to zero is—

$$\delta n \mathrm{RT} \log \frac{[Na^{\cdot}]_{II}}{[Na^{\cdot}]_{I}} + \delta n \mathrm{RT} \log \frac{[Cl']_{II}}{[Cl']_{I}} = 0,$$

or

$$[Na^{\cdot}]_{II} \times [Cl']_{II} = [Na^{\cdot}]_{I} \times [Cl']_{I} \quad . \quad . \quad . \quad (1)$$

where the square brackets denote concentration terms. It is unnecessary to take into consideration any potential difference which may exist between the two sides of the membrane, since equivalent quantities of positive and negative electricity have been transferred from II. to I. If we carry out an exactly similar work process for the undissociated NaCl molecules from II. to I. we get—

$$\delta n \mathrm{RT} \log \frac{[NaCl]_{II}}{[NaCl]_{I}} = 0,$$

or

$$[NaCl]_{I} = [NaCl]_{II}.$$

Combining this equation with the former similar relation for the ions, we obtain—

$$\frac{[Na^{\cdot}][Cl']}{[NaCl]} = \text{constant},$$

i.e. the Law of Mass Action, which is known to be contrary to experience (at least if the ordinary conductivity method of determining degree of dissociation be taken as giving correct values). Donnan considers the discrepancy may be due to the abnormality of the undissociated molecules and that equilibrium across the membrane need not necessarily conform to the criterion that $[NaCl]_{II} = [NaCl]_{I}$. Returning to equation (1), since in general $[Na^{\cdot}]_{I}$ is not equal to $[Na^{\cdot}]_{II}$, because the $Na^{\cdot}$ is obtained by the dissociation of both NaR and NaCl, it follows that $[Cl']_{I}$ is not equal to $[Cl']_{II}$. To get at some more quantitative relation, one may make the following simplifying assumptions :—

(*a*) Complete electrolytic dissociation of NaR and NaCl.

(*b*) Equal volumes of liquid on each side of the membrane.

We can thus represent the initial and equilibrium states as follows :—

Initial State.				Equilibrium State.				
I.		II.		I.			II.	
$Na^{\cdot}$	R'	$Na^{\cdot}$	Cl'	$Na^{\cdot}$	R'	Cl'	$Na^{\cdot}$	Cl
c_1	c_1	c_2	c_2	$c_1 + x$	c_1	x	$c_2 - x$	$c_2 - x$

where the symbols c_1, c_2 represent gram-ions per liter. That is $\frac{x}{c_2}100$ represents the percentage of NaCl which has diffused from II. into I., and $\frac{c_2 - x}{x}$ the equilibrium distribution ratio of the sodium chloride between I. and II.

Equation (1) can now be written in the form—

$$(c_1 + x)x = (c_2 - x)^2$$

or

$$x = \frac{c^2_2}{c_1 + 2c_2}$$

whence

$$\frac{x}{c_2} = \frac{c_2}{c_1 + 2c_2}$$

$$\frac{c_2 - x}{x} \cdot \frac{c_1 + c_2}{c_2}.$$

If c_2 is small compared to c_1, one may write—

$$\frac{x}{c_2} = \frac{c_2}{c_1} \text{ and } \frac{c_2 - x}{x} = \frac{c_1}{c_2}.$$

By way of illustration, suppose $c_2 = \frac{c_1}{100}$, then $\frac{x}{c_2} = \frac{1}{100}$, or only 1 per cent. of the NaCl originally present in II. diffused into I. If on the other hand, c_1 is small compared to c_2, it follows that—

$$\frac{x}{c_2} = \frac{1}{2} \text{ and } \frac{c_2 - x}{x} = 1, \text{ as one would expect.}$$

The following table shows the variation of the distribution of sodium chloride between the solutions as a function of the concentration of the NaR and NaCl itself :—

Initial Concentration of NaR in I.	Initial Concentration of NaCl in II.	Initial Ratio NaR | NaCl.	Percentage of NaCl Diffused from II. to I.	Distribution Ratio of NaCl between II. and I. when Equilibrium is Reached.
c_1.	c_2.	c_1/c_2.	$100\frac{x}{c_2}$.	$\frac{c_2 - x}{x}$.
0·01	1	0·01	49·7	1·01
0·1	1	0·1	47·6	1·1
1	1	1	33	2·0
1	0·1	10	8·3	11·0
1	0·01	100	1·0	99·0

The equilibrium reached is naturally independent of the assumption that the NaCl was initially in II. The same equilibrium point would be reached if the NaCl had been initially in I. The table shows that the influence of the non-dialysing NaR upon the distribution of the NaCl is extremely great. Although the membrane is quite permeable

to NaCl, the presence of NaR in sufficient concentration on one side is able to make the permeability of the membrane for NaCl in *one direction* almost vanish. Donnan points out that such effects must be of great importance in physiology, for in living tissues membranes are always present and the existence of protein salts which correspond to the hypothetical substance NaR will evidently have a very marked effect upon the distribution of simple inorganic salts to which these membranes are "normally" perfectly permeable. The unequal distribution of NaCl on two sides of parchment owing to the presence on one side of Congo red, has been experimentally demonstrated by Harris in Donnan's Laboratory.

Influence of the Unequal Distribution on the Measurement of Osmotic Pressure.

It follows from what has been said that no direct measurement of the osmotic pressure of NaR can be made in the presence of NaCl owing to the opposing pressure exerted by the NaCl, *i.e.* owing to the difference of osmotic pressure of the NaCl in II. and in I. Assume for simplicity's sake that the salts are all completely dissociated and equal volumes of solution are present on each side of the membrane. The *true* osmotic pressure of the NaR is then given by the equation—

$$P_0 = 2c_1RT.$$

If we call P the opposing pressure of the NaCl, we have—

$$P = 2(c_2 - x)RT - 2xRT \text{ or } 2(c_2 - x - x)RT.$$

The observed osmotic pressure of the NaR in I. is P_1, where—

$$P_1 = P_0 - P = 2RT(c_1 - (c_2 - 2x)) = 2RT(c_1 - c_2 + 2x).$$

Hence

$$\frac{P_1}{P_0} = \frac{c_1 + c_2}{c_1 + 2c_2}$$

since

$$x = \frac{c^2_2}{c_1 + 2c_2}.$$

If c_1 is small compared to c_2, then $P_1 = \frac{1}{2}P_0$. If c_2 is small compared to c_1, then $P_1 = P_0$, as one would expect. The following table illustrates these relationships :—

$\frac{c_2}{c_1}$.	$\frac{P_1}{P_0}$.
0·1	0·92
1	0·67
2	0·60
10	0·52

On account of the unequal distribution an addition of an electrolyte with a common ion will diminish the true osmotic pressure of an

electrolytically dissociated non-dialysing substance. This has been experimentally verified by Harris.

The Case of an Electrolyte without an Ion in Common with the Non-dialysing Substance.

This can be treated in exactly the same way as the simpler case. Suppose in solution I. we have the substance NaR (dissociated) and in II. the salt KCl also dissociated. Then the initial concentration will be represented by—

$Na^{\cdot}$	R'		$K^{\cdot}$	Cl'
c_1	c_1	|	c_2	c_2
I.			II.	

The ions of KCl diffuse from II. into I., and the ions of NaCl can diffuse now from I. into II. The equilibrium state will thus be represented by—

$Na^{\cdot}$	$K^{\cdot}$	Cl'	R'		$K^{\cdot}$	$Na^{\cdot}$	Cl'
$c_1 - z$	x	y	c_1	|	$c_2 - x$	z	$c_2 - y$

In order to have electric neutrality on either side, it is necessary that $z = x - y$. By considering the work done in small virtual changes at the equilibrium point, the following relation is obtained as a criterion of equilibrium :—

$$\frac{[Na^{\cdot}]_I}{[Na^{\cdot}]_{II}} = \frac{[K^{\cdot}]_I}{[K^{\cdot}]_{II}} = \frac{[Cl']_{II}}{[Cl']_I} = \frac{c_1 + c_2}{c_2} = R.$$

Taking the case in which $\frac{c_1}{c_2} = 100$, the following changes from the initial state will take place—

(*a*) 99 per cent. of the $K^{\cdot}$ originally present in II. will diffuse into I.

(*b*) Only 1 per cent. of Cl' originally present in II. will diffuse into I.

(*c*) Only 1 per cent. of $Na^{\cdot}$ originally present in I. will diffuse into II.

It will again be surprisingly evident how great an effect the substance NaR has upon the ionic distribution of KCl on the two sides of the membrane. In this case there has apparently been an exceedingly marked preferential effect, nearly all the $K^{\cdot}$ being "drawn" into I. and Cl' expelled. This latter phenomenon would be realised if the KCl had been present in I. to start with.

Hydrolytic Decomposition of Salts by the Membrane.

The question which now arises is: What will happen if on one side of the membrane there is NaR and on the other pure water? The $Na^{\cdot}$ will tend to pass through the membrane since the latter is permeable to this ion, but this can only take place if at the same time an equivalent

quantity of OH' (from the water) diffuses in the same direction. The initial and final states could be represented thus—

Initial State.				Equilibrium State.	
$Na^\cdot$	R'	pure water	$Na^\cdot$		$Na^\cdot$
			$H^\cdot$		
			R'		OH'
I.		II.	I.		II.

The solution in compartment I. will thus become acid. To find the equilibrium concentration relations let us assume that equilibrium is reached and that a small virtual change is made involving the transfer of δn moles of $Na^\cdot$ from I. to II. and δn moles of OH' from I. to II. This leads to the relation—

$$\delta n \mathrm{RT} \log \frac{[Na^\cdot]_I}{[Na^\cdot]_{II}} + \delta n \mathrm{RT} \log \frac{[OH']_I}{[OH']_{II}} = 0$$

whence

$$\frac{[Na^\cdot]_I}{[Na^\cdot]_{II}} = \frac{[OH']_{II}}{[OH']_I}.$$

In order to make the consideration of the problem as simple as possible, we assume the following :—

(*a*) Complete electrolytic dissociation of all electrolytes present (with the exception of water naturally).

(*b*) I. and II. occupy equal volumes.

(*c*) The $H^\cdot$ ions produced in I. at the equilibrium state (or the OH' produced in II.) are in relatively great concentration compared to the concentration of the same ions produced from water under ordinary circumstances. We may thus write down the following concentration relations :—

Initial State.			Equilibrium State.				
$Na^\cdot$	R'	pure water.	$Na^\cdot$	$H^\cdot$	R'	$Na^\cdot$	OH'
c_1	c_1		$c_1 - x$	x	c_1	x	x
I.		II.	I.			II.	

The equilibrium relation above may thus be written—

$$\frac{c_1 - x}{x} = \frac{x}{[OH']_I}.$$

Also if K_w denotes the ionisation constant for water, then—

$$x \times [OH']^I = K_w.$$

Eliminating the $[OH']_I$ term, one obtains—

$$x^3 = K_w(c_1 - x).$$

If x is small compared to c_1 we obtain the very simple relation—

$$x = \sqrt[3]{K_w c_1}.$$

This equation predicts very small values for x, which only increase relatively slowly with increase in c_1. The following table shows the nature of the results obtained for the temperature 25° C. ($K_w = 10^{-14}$) :—

c_1.	x.	$\frac{100x}{c_1}$.
0·01	5×10^{-6}	0·05 per cent.
0·1	1×10^{-5}	0·01 ,,
1	2×10^{-5}	0·002 ,,

The degree of hydrolytic dissociation $\frac{x}{c_1}$ brought about by the chemically "*in*active" membrane is extremely small. The remarkable thing is that there should be any hydrolysis at all, especially as we are considering the case of complete dissociation which means that the acid and base forming NaR are both strong, as otherwise the $H^{\cdot}$ present finally would react with R′ to form undissociated (weak) acid. These simple considerations, however, show that the hydrolysis must actually take place, a fact which has been experimentally verified by Harris in Donnan's Laboratory. By increasing the volume of II. in comparison to I. the degree of hydrolysis can be increased. If, for example, the volume of II. is made v times greater than that of I., we must write the equilibrium conditions as follows:—

$Na^{\cdot}$	$H^{\cdot}$	R'	$Na^{\cdot}$	OH'
$c_1 - x$	x	c_1	$\frac{x}{v}$	$\frac{x}{v}$
I.			II.	

the corresponding equations being—

$$x^3 = K_w v^2 (c_1 - x)$$

or when x is small compared to c_1—

$$x = \sqrt[3]{K_w v^2 c_1}.$$

If, for example, $v = 100$, $c_1 = 0{\cdot}1$, then x will be of the order 10^{-4}, so that the percentage hydrolysis $\frac{100x}{c_1}$ will be of the order 0·1. Naturally if the acid HR is a weak acid this will reduce the $H^{\cdot}$ concentration in I. and will tend to increase the membrane hydrolysis. Donnan has worked out this case when K_a, the dissociation constant of the acid HR, is small. It is found (for details the original paper may be consulted) that the degree of hydrolysis may be written—

$$x^3 = \frac{K_w}{K_a}(c_1 - x)(c_1 - 2x).$$

If x is small compared to c_1, one obtains—

$$x = \sqrt[3]{\frac{K_w}{K_a} c_1^2}.$$

As an example of the numerical values likely to be obtained, putting

$c_1 = 1$, $K_w = 10^{-14}$, and $K_a = 10^{-5}$, then $x = 10^{-3}$, and $\frac{100.x}{c_1} = 0{\cdot}1$, *i.e.* 0·1 per cent. hydrolysis. Such hydrolytic effects must take place in the ordinary process of dialysis and must also be present when measurements of osmotic pressure of electrolytic colloids are made by means of membranes.

Experimental Evidence for the Foregoing Theory.

As illustrating the kind of evidence which can be brought forward, for the three membrane effects hitherto considered, *viz.* (1) the unequal distribution of a simple electrolyte on the two sides of a membrane ordinarily quite permeable to the electrolyte, when an electrolytic colloid is present on one side of the membrane; (2) the influence of this unequal distribution on the apparent osmotic pressure of the colloid; (3) the hydrolysis of the electrolytic colloid by the chemically inert membrane—a short account will be given of certain of the experimental results obtained by Donnan and Harris (*Trans. Chem. Soc.*, **99**, 1554 (1911)) in connection with the osmotic behaviour of Congo red (the sodium salt of diphenylbisazonaphthylamine sulphonic acid).

The osmometer employed was fitted with parchment paper membranes, which are ordinarily quite permeable to the molecules and ions of salts, such as NaCl, but are impermeable, or practically so, to the molecule and anion of a substance such as Congo red. In the first series of experiments measurements of the osmotic pressure were made with solutions of Grübler's Congo red, which was found to contain about 30 per cent. of NaCl. A liter of distilled water, free from CO_2, formed the liquid external to the osmometer cell, which cell contained the dyestuff. On setting up the cell the following general behaviour was observed. The pressure rose quickly at first, the velocity of increase gradually diminishing. After four or five days the pressure attained a maximum, and then began slowly to decrease. On changing the external water a further rise in pressure occurred, followed by a slow fall. Succeeding changes of the external water gave rise to the same phenomenon, the increase of pressure becoming, however, rapidly smaller with each successive change of external water. The experiments were carried out at 17° C. It was found that the orginal liter of water contained nearly all the NaCl present initially in the Congo red, the second liter removing practically the whole of the remainder.

In order to get a clear idea of what is occurring in the above rather complex behaviour, Donnan and Harris proceeded to show in the first place that the NaCl, when it has reached equilibrium, becomes unequally distributed, that is, that its concentration in the external water becomes greater than in the osmometer vessel, thus producing an osmotic pressure opposed to that of the Congo red. This was shown in the following way :—

Five grams of Merck's Congo red, containing 16·47 per cent. sodium (showing therefore the presence of a fairly large amount of foreign

electrolytes, NaCl and Na_2SO_4) were dissolved in 200 c.c. of distilled water, free from CO_2, and placed inside a parchment tube, suspended in a liter of pure distilled water. By means of three changes of water the greater portion of the admixed salts was removed, dialysis being continued for twenty-four hours. Then the outer water was replaced by a liter of N/10 NaCl. After thirteen days the chlorine content of the inside and outside liquids was determined. The results are as follows:—

Outer liquid, 5·106 grams NaCl per liter.
Inner liquid, 4·478 „ „ „ „

The concentration of the Congo red was 1·074 per cent. This experiment shows that after thirteen days dialysis, the concentration of the NaCl in the outer solution is undoubtedly greater than that in the inner. In order to meet the objection that in the above experiment the NaCl might still have been diffusing into the inner solution, two further experiments were made in which the concentration of the NaCl was initially higher in the inner solution, containing the Congo red, than in the outer liquid.

In the first of these a mixture of approximately 2·8 grams pure Congo red and 7·2 grams NaCl dissolved in 200 c.c. of conductivity water were placed inside the dialysis and a liter of pure water outside. After six days' dialysis the inner liquid contained 5·136 grams NaCl per liter, the outer liquid 5·728 grams per liter, the concentration of the Congo red (in the inner) being 0·917 gram per 100 c.c. In the other experiment the inner solution consisted initially of about 2·1 grams pure Congo red and 3·9 grams of NaCl in 200 c.c. of water, the outer liquid being 1 liter of water. After five days' dialysis the inner liquid contained 2·53 grams NaCl per liter, the outer 3·03 grams per liter, the concentration of Congo red (in the inner) being 0·875 gram per 100 c.c. These results show that the equilibrium is a reversible one, and that the equilibrium state corresponds to a greater concentration of NaCl on the opposite side of the membrane to the Congo red. This unequal distribution will set up, in the osmotic pressure experiments, a counter pressure which will make the observed osmotic pressure *lower* than the true one possessed by the Congo red. When the external water is changed in the osmotic experiments this counter pressure is removed and thus a sensible rise of osmotic pressure occurs; that is, in the limit, the true osmotic pressure due to the Congo red is observed.

The following calculation serves to indicate the amount of counter pressure referred to. Consider the first of the three experiments cited above, namely, that in which the parchment tube, immersed initially in a liter of N/10 NaCl, was found to contain finally 5·106 grams NaCl per liter. The osmotic pressure at 0° C. of the outer solution of NaCl is

$$22{\cdot}4 \times 760 \times \frac{3{\cdot}106}{58{\cdot}5} \times i \text{ mm. mercury,}$$

where i is van 't Hoff's factor for a solution of this concentration. The osmotic pressure due to the NaCl concentration in the inner solution is—

$22{\cdot}4 \times 760 \times \frac{4{\cdot}478}{58{\cdot}5} \times i'$. Setting $i = i' = 1{\cdot}85$, we get for the counter osmotic pressure at 17° C.—

$$22{\cdot}4 \times 760 \times \frac{290}{273} \times \frac{0{\cdot}628}{58{\cdot}5} \times 1{\cdot}85 = 359 \text{ mm. mercury.}$$

Now the osmotic pressure at 17° C. of the Congo red solution present in this experiment, namely, 1·074 per cent. Congo red, would amount to 290 mm. mercury. Hence the approximately N/12 solution of NaCl would more than suffice to annul the osmotic pressure of the 1·074 per cent. Congo red solution.

Returning to the original osmotic behaviour of the Congo red solution, we have still to account for the gradual decrease in pressure exhibited after a maximum has been attained. Donnan explains this on the basis of membrane hydrolysis. In the osmometer experiments Donnan and Harris point out that the contents of the osmometer acquire a muddy brown appearance after about forty-eight hours' dialysis. This appears to be due to the presence of a fine colloidal suspension. This solution is unaffected by a small quantity of NaCl, whereas a trace of NaOH reconverts it into the original bright red solution. The turbidity is regarded as colloidal Congo red acid or the acid salt, possibly containing adsorbed Congo red. The gradual formation of this would give a satisfactory explanation of the gradual fall in the osmotic pressure. The acid has been formed by the passage outwards of some Na^+, along with OH^-, leaving an equivalent number of H^+ ions in the osmometer. If this is the case we should be able to prevent this membrane hydrolysis, and so obtain a constant osmotic pressure by employing, instead of pure water, a dilute solution of NaOH as the outer liquid. This is confirmed by experiment. The value of the osmotic pressure when the Congo red is dilute approaches closely to that calculated for simple undissociated molecules. With more concentrated solutions of Congo red its colloidal behaviour manifests itself, aggregation occurring, so that the osmotic pressure per molecule decreases with increasing concentration.

The gradual hydrolysis of Congo red solutions on dialysis with continued change of the outer liquid was conclusively shown by determinations of the sodium content of the inner liquid. Thus, in a certain case, starting with impure Congo red, after four days' dialysis the sodium content of the inner liquid was found to be practically that corresponding to pure Congo red, namely 6·6 per cent. of the dried solid. After three weeks' dialysis the sodium content of the dried residue, obtained on evaporation, was found to be 6·0 per cent., thus indicating a loss of sodium from the inner liquid. In order to obtain a more marked difference, a diluted solution of the muddy brown liquid, obtained after three weeks' dialysis, was subjected to further dialysis with daily removal of the external water. After seven weeks' dialysis the muddy solution in the dialyser had assumed a violet hue, and the dried residue was now found to contain only 1·6 per cent. of sodium. As indicating the reversibility

of the change in the dyestuff it was found that a portion of this violet solution, when boiled in a beaker, abstracted enough alkali from the glass to become converted into the normal Congo red salt. Similar results, as regards removal of sodium, were obtained more rapidly with Kahlbaum benzopurpurine—4B.

In a later paper (*Trans. Chem. Soc.*, **105**, 1941 (1914)) Donnan and Allmand investigated the distribution equilibrium of potassium and chlorine ions across a copper ferrocyanide membrane. The results, whilst confirming the theory, were complicated by the uncertainty as to the manner of ionisation of potassium ferrocyanide. It was considered that this difficulty would be overcome if solutions of two ferrocyanides were employed on the two sides of the membrane, especially if these salts were ionised to the same extent. This case was investigated by Donnan and Garner (*Trans. Chem. Soc.*, **115**, 1313 (1919)).

With a mixture of potassium and sodium ferrocyanides equilibrium will be set up by an interchange of sodium and potassium ions, since the membrane is not permeable to ferrocyanogen ions. The theory applicable in this case has been given in the section dealing with "the case of an electrolyte without an ion in common with the non-dialysing substance," the condition for equilibrium being—

$$[Na^+]_I \times [K^+]_{II} = [Na^+]_{II} \times [K^+]_I$$

assuming that the ions obey the laws of ideal solutions, that is, assuming that their activities (Chap. VIII.) are sensibly the same as their concentrations. When calcium ferrocyanide is used in place of potassium ferrocyanide the equilibrium should be defined by—

$$[Ca^{++}]_I \times [Na^+]^2_{II} = [Ca^{++}]_{II} \times [Na^+]^2_I \quad . \quad . \quad (a)$$

and

$$[Ca]_I \times [Na]^2_{II} = [Ca]_{II} \times [Na]^2_I \quad . \quad . \quad . \quad (b)$$

if the degree of ionisation of the two salts is the same.

In the case of the sodium-potassium osmotic cells the experimental results showed good agreement with the requirements of the theory. The solutions were 0·025 molar, the volume of each cell being 100 c.c. The usual procedure was to place a solution of potassium ferrocyanide in one side of the cell, and the sodium ferrocyanide in the other. The time required for the attainment of equilibrium was determined by conductivity measurements, and no further change in the conductivity could be observed after an interval of one week. The cells were, however, allowed to remain in darkness, with occasional shaking, for three to five weeks, in which time equilibrium was certainly reached. Ultimately the contents of the solutions on each side of the membrane were analysed. The results are given in the following table. The column headed Na and K give the total concentration of these constituents. The ratio Na/K is given in the final column, and it will be observed that the ratio is the same for compartment *a* as for compartment *b* within the experimental error. It is assumed that the ratio of the ionic concentrations will be practically the same as those given in the table, since the sodium and potassium salts are similar in character.

Cell No.	Normality of		Na/K.
	Na.	K.	
1 *a*	0·0335	0·0451	0·743
b	0·0410	0·0567	0·723
2 *a*	0·0503	0·0497	1·012
b	0·0496	0·0498	0·996
3 *a*	0·0516	0·0477	1·082
b	0·0575	0·0524	1·097
4 *a*	0·0559	0·0443	1·262
b	0·0666	0·05205	1·280
5 *a*	0·0573	0·0416	1·377
b	0·0884	0·0643	1·375

In the case of the sodium-calcium ferrocyanide solutions a somewhat unexpected result was obtained. Whereas equation (*b*), which refers to the concentrations of the two salts, holds within the limit of experimental error, it was found that equation (*a*) does not accurately represent the relationship between the ionic concentrations of the calcium and sodium salts on the two sides of the membrane. The activities of the ions in this case appear to be more closely related to the molar than to the ionic concentrations. The difficulty here encountered is not to be regarded as a failure of Donnan's theory of distributional equilibrium, but a failure in the means possessed at the present time for determining with accuracy the true activities of ions.

Experiments were also carried out by Donnan and Garner with a *liquid* membrane, namely amyl alcohol, the solutes being LiCl and KCl. LiCl is easily soluble in amyl alcohol, whilst KCl is only very slightly soluble. The osmotic cell system in this case would be represented by—

KCl and LiCl in water | amyl alcohol | LiCl in water.

The problem has to be dealt with indirectly, owing to the too slow diffusion of LiCl through the alcohol. The results, so far as they have gone, substantiate the theory. For details the original paper must be consulted.

"*Membrane Potential*" (the P.D. existing when the equilibrium as modified by the membrane is reached).

Consider the simplest case of a NaR and NaCl, equilibrium being represented by—

$Na^{\cdot}$	$Na^{\cdot}$
R'	
Cl'	Cl'
I.	II.

Let π_1 and π_2 be the potentials (for positive electricity) of the solutions I. and II. Suppose the extremely small mass $F\delta n$ of positive electricity be transferred isothermally from II. to I., then in this virtual change of the system from the equilibrium the following work terms must be considered:—

(*a*) Change in free electrical energy $= F\delta n(\pi_2 - \pi_1)$.

(*b*) $p\delta n$ moles of $Na^{\cdot}$ ions has been transferred from II. to I. and simultaneously $q\delta n$ moles of Cl' ion from I. to II., where $p + q = 1$ (*i.e.* p and q represent the fraction of the total current carried by the respective ion, or in other words p and q are the transport numbers of the ions). The maximum osmotic work of operation (*b*) is given by—

$$p\delta nRT \log \frac{[Na^{\cdot}]_{II}}{[Na^{\cdot}]_{I}} + q\delta nRT \log \frac{[Cl']_{I}}{[Cl']_{II}}.$$

Now since the system is in equilibrium the electrical virtual work must balance the osmotic virtual work, or—

$$F\delta n(\pi_1 - \pi_2) = p\delta nRT \log \frac{[Na^{\cdot}]_{II}}{[Na^{\cdot}]_{I}} + q\delta nRT \log \frac{[Cl']_{I}}{[Cl']_{II}}.$$

Now we have seen that in this case in the equilibrium state the following relation holds—

$$\frac{[Na^{\cdot}]_{II}}{[Na^{\cdot}]_{I}} = \frac{[Cl']_{I}}{[Cl']_{II}} = \lambda \text{ say,}$$

and also $p + q = 1$.

Hence it follows that—

$$\pi_1 - \pi_2 = \frac{RT}{F} \log \lambda.$$

For the simple case investigated we see that—

$$\lambda = \frac{x}{c_2 - x} = \frac{c_2 - x}{c_2 + x},$$

where $x = \frac{c^2_2}{c_1 + 2c_2}$.

So that the potential difference E across the membrane due to the distribution of ions is—

$$E = \pi_2 - \pi_1 = \frac{RT}{F} \log \frac{I}{\lambda} = 0{\cdot}058 \log \frac{c_1 + c_2}{c_2}$$

$$E = 0{\cdot}058 \log \left(1 + \frac{c_1}{c_2}\right).$$

If c_2 is small compared to c_1 it follows that—

$$E = 0{\cdot}058 \log \frac{c_1}{c_2}.$$

If, on the other hand, c_1 is small compared to c_2, the potential difference approximates to zero, as one would expect, for in the limit in which

there is no NaR present at all the NaCl will distribute itself in equal concentration on each side of the membrane. The following table illustrates the numerical values of E for a series of arbitrarily chosen c_1 and c_2 values:—

$\frac{c_1}{c_2}$.	E.
1	+ 0·017
10	+ 0·060
100	+ 0·116
1000	+ 0·174

In a similar manner one may calculate the potential differences in the more general case in which KCl is present in place of NaCl.

Theory of Vegetable Tanning.

The theory of tanning, given below, is that suggested by Procter and Wilson (*Trans. Chem. Soc.*, **109**, 1327 (1916)). The actual words of the original investigators have been extensively employed. The treatment of the problem as will be seen is essentially an application of Donnan's theory of membrane potential, which we have just considered. Further, the considerations are of a general kind, not necessarily restricted to the process of tanning alone; they suggest, indeed, a general treatment of colloidal equilibrium and precipitation from the electrical standpoint (*cf.* Wilson, *Journ. Amer. Chem. Soc.*, **38**, 1982 (1916)), and may be applied to processes such as dyeing. The fundamental assumption is, that a colloid owes its stability to the formation of an ionisable complex between the particles of the disperse phase and certain substances present in the medium (*cf. inter alia*, the investigations of Beans and Eastlack referred to in the chapter on Colloids in Vol. I.).

The process of tanning is regarded as a "combination" of tannins with hide fibre; the principal constituent of the fibre for our present purpose being the colloidal substance, collagen. The object of the theory is to offer an explanation of the influence of acids, bases, and slats upon the tanning process, it being assumed that neutralisation of the electric charge is the direct cause of the union of the tannin with the fibre. In the light of our earlier considerations (Vol. I.) we cannot regard this electrical view as a final statement of the whole process of tanning, *i.e.* capillary effects will eventually have to be allowed for, though this does not invalidate the important advance made by the present electrical theory.

The tannins dissolve in water forming colloidal sols, in which the individual particles are negatively charged, so that, on the present view, the surface layer immediately surrounding the particles (referred to hereafter as the surface layer) must contain a certain concentration of positive ions bound by electrochemical attractions to the negatively

charged tannin. The tannin may acquire its charge by combining with a negative ion or by ionising, as do soaps or Congo red; it is immaterial to the theory whichever is the case. Call the concentration of tannin particles [T'] and that of the positive ions bound by electrical attractions to the tannin [M^+], and let some of the electrolyte MN be added to the solution. (For the sake of simplicity we are considering the case of a binary electrolyte of the uni-univalent type. Procter and Wilson show that the theory is equally applicable to any type of electrolyte.) In the surface layer there will be a certain concentration of M^+ ions bound by electrochemical attractions to the tannin, as well as some M^+ and N^- not so bound, so that in this layer [M^+] and [N^-] will be unequal, whilst in the bulk of the solution they will necessarily be equal; a condition to which Donnan's work on membrane equilibria is applicable.

When equilibrium is established, if a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged, that is, no work will be done. The change here considered is the transfer of δn moles of M^+ and N^- from the bulk of the solution to the surface layer. The condition of equilibrium is then:—

$$\delta n \mathrm{RT} \log \frac{[M^+]_{II}}{[M^+]_I} + \delta n \mathrm{RT} \log \frac{[N^-]_{II}}{[N^-]_I} = 0$$

where $[M^+]_{II}$ represents the concentration of M^+ in the bulk of the solution and $[M^+]_I$ its concentration in the surface layer.[1] It follows from the preceding equation that at equilibrium—

$$[M^+]_{II} \times [N^-]_{II} = [M^+]_I \times [N^-]_I.$$

In words, if only binary electrolytes are present, the products of concentration of any pair of diffusible and oppositely charged ions will be equal in surface layer and bulk of solution.

The following system of notation has been adopted by Procter and Wilson to keep the reasoning as closely allied as possible to that of earlier papers (referred to in *Trans. Chem. Soc.*, **109**, 1327 (1916)).

In the bulk of the solution, let

x = concentration of positive or negative ions.

In the surface layer, let

y = concentration of negatively charged diffusible ions.

z = concentration of positively charged ions bound by electrochemical attractions to the tannin.

Then, $y + z$ = concentration of positively charged ions.

From the law of equality of products just derived, it follows that

$$x^2 = y(y + z).$$

The different distribution of ions in the surface layer and bulk of solution will result in a difference of potential, the formula for which is given by Donnan as follows:—

[1] In view of the recent work on dilute solutions of strong electrolytes discussed in Chap. VIII., the above equation must be slightly in error, because in it the gas law is assumed for the ions. Judging by Bates' results, however, the error in the case of ions is not large; in the case of molecules it is very considerable.

$$E = \frac{RT}{F} \log I/\lambda.$$

In the present case,

$$\lambda = y/x = \frac{-z + \sqrt{4x^2 + z^2}}{2x}.$$

We may write therefore,

$$E = \frac{RT}{F} \log \frac{2x}{-z + \sqrt{4x^2 + z^2}}$$

where z is either a constant or has a limiting maximum value, *viz.* the maximum concentration of positively charged ions which will be held by the colloid tannin particles. Hence,

$$\lim_{x = \infty} E = \frac{RT}{F} \log \frac{2x}{\sqrt{4x^2}} = 0$$

proving that *the potential difference existing between surface layer and bulk of solution will diminish as the concentration of electrolytes in the solution is increased.* When this difference of potential has been made sufficiently small, by addition of electrolytes, a condition is established which is favourable to the coalescence of the particles, and consequently the tannin precipitates. (In Vol. I. we have seen that there are apparent exceptions to this simple electrical view.)

When hide is immersed in an *acid* solution, a highly ionisable salt of collagen is formed in which the collagen is *positively* charged, and therefore this potential difference will be expressed by the formula

$$E = \frac{RT}{F} \log \frac{-z + \sqrt{4x^2 + z^2}}{2x}$$

where E is obviously of opposite sign to that in the case of tannin. In *alkaline* solution hide substance reacts with the resulting formation of ionisable salts, the collagen now being *negatively* charged, in which case E would have the same sign as in the case of tannin.

If therefore a hide is immersed in a slightly *acid* solution of tannin, as the tannin particles approach the substance of the hide, electrical neutralisation with the resulting co-precipitation of the two colloids must follow. This, according to Procter and Wilson, is the fundamental action of vegetable tanning. Various tannins, however, differ chemically from one another, and consequently all would not produce the same value for z under a fixed set of conditions. The greatest difference of potential between surface layer and bulk of solution will be found in those tannins in which z has the greatest value. Such tannins would combine most rapidly with the hide and form the most stable leather, but would not be suited for use excepting with hide which had been almost completely tanned. Procter and Wilson suggest that the determination of z for various tannins would be a useful index of their merit.

The rate of tanning will be a maximum for a given concentration of liquor when the potential differences are of opposite signs and the ab-

solute value of each is a maximum. As the concentration of electrolytes in the solution is increased, the potential differences between the solution and the collagen phase, and between the solution and the layer round the tannin, will decrease, thereby lessening the rate of tanning; but if the concentration of electrolytes is increased sufficiently, the tannin must precipitate alone and the collagen shrink to a hard mass. In alkaline solutions both colloids have negative charges, and consequently will not combine, whilst in the presence of lime the negatively charged tannin particles are neutralised by calcium ions and a calcium compound of the tannin precipitates. This reasoning clears up many points concerning the function of acids in tan liquors, and the important *rôle* played by salts in the process. Analogous effects may be explained in a similar manner in other processes which involve colloids.

The Micelle Theory of Colloidal Electrolytes.

(Compare the summarising paper by McBain and Salmon, *Journ. Amer. Chem., Soc.*, **42**, 426 (1920), from which the following account is directly taken.)

Colloidal electrolytes are salts in which an ion has been replaced by a heavily hydrated polyvalent micelle, consisting chiefly of agglomerated anions, each micelle carrying an equivalent sum total of electrical charges and conducting electricity as well or even better than the simple ion which it replaces. The chief feature of the micelle is its great electrical mobility, which it possesses in virtue of the numerous charges upon it, and at the same time its very low mechanical mobility, which it possesses in virtue of its great mass and hydration, thereby giving rise to marked viscosity on the part of the solution.

In a measure, the properties of this ionic micelle must apply to all colloids which possess even slight electrical charges. In the case of proteins and soaps at high concentration, the undissociated substance is an ordinary colloid while the organic ion is a micelle. In dilute soap solutions, on the other hand, the undissociated molecules possess only the simple formula weight and the ions are also simple. The class called electrolytic colloids, characterised by the existence of the micelle is extremely wide, embracing such substances as acid and alkali proteins, dyes, indicators, sulphonates and soaps. The work of McBain and his collaborators extending over several years and cited in the paper referred to, deals mainly with the properties of soap solutions. We shall consider such systems from the standpoint of the micelle.

McBain and Taylor have found that soap solutions are characterised by possessing high electrical conductivity. This shows that they consist to a large extent of something other than neutral colloid. The next step was to show, by two independent methods, namely by the rate of catalysis and the e.m.f. of the hydrogen electrode, that the hydroxyl ion present was negligible, its concentration being only about 0·001N. Hence the high conductivity was due to the soap itself.

In addition to electrical conductivity measurements a long series of determinations of the molecular weights of soap solutions have been

carried out, the results of which demonstrate that as the soap solutions become more dilute there is a gradual transition from colloid to crystalloid. This refers to the undissociated colloid as well as the colloidal anion or micelle. A dilute solution of soap is essentially an electrolyte like sodium acetate. Quite definite and reproducible equilibria are set up between the various constituents, colloid and crystalloid. The experimental method of determining the concentration of the various constituents in any solution consisted in a modification of the dew-point method of molecular weight determination first employed by Cumming (*Trans. Chem. Soc.*, **95**, 1772 (1909)). Some details of this method are given in the next section.

Dew-point Method of Determining the Molecular Weight of a Solute.

In connection with soap solutions it is impossible to use the ordinary boiling point method owing to the presence of a large amount of air which does not escape from the bubbles and therefore by its partial pressure, invalidates the results. This is a criticism of Krafft's well-known boiling point observations on soap solutions, and equally invalidates

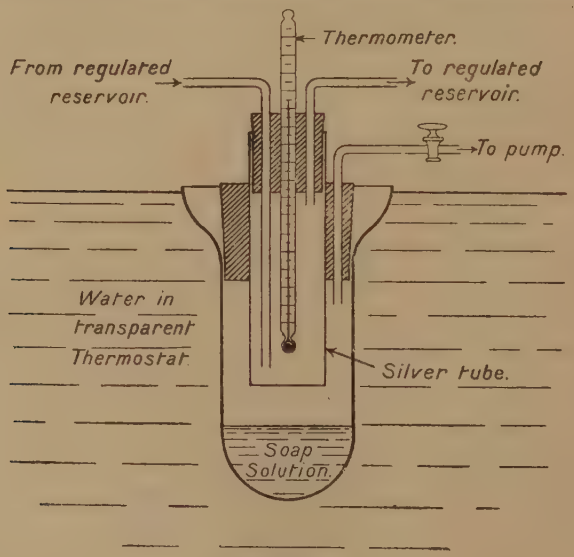


FIG. 50 (*a*).

Smits tensimeter measurements. Correct vapour pressure measurements can be obtained with special precautions.

The dew-point apparatus of McBain is as shown in the Fig. 50 (*a*).

A highly-polished silver tube with silver bottom is closed with a cork at the top. Through the cork are inserted a thermometer and two tubes through which a rapid current of water is circulated by a pump

from and to a thermostat of adjustable temperature. The silver tube is held in a cork in a glass vessel which contains the solution to be studied. The top of the glass vessel rises an inch or so above the cork so that the enclosed space is completely immersed in the water of a thermostat with glass sides. Further, a capillary glass tube passes through the cork holding the silver tube and can be connected with a pump and thus evacuated or the pressure adjusted to any desired value. This tube is closed by a glass tap.

The principle of the method is as follows. When the silver tube is cooled by running water through it, just far enough to form a little dew, the pure water thus formed on the surface of the tube is in equilibrium with the vapour over the solution. The vapour pressure can therefore be obtained from tables giving the saturated vapour pressure of water as a function of temperature. But this vapour is also in equilibrium with the soap solution, which solution is at a somewhat higher temperature, namely, that of the transparent thermostat. In other words, the difference of temperature between the silver tube and the soap solution is the rise in boiling point of water, at reduced pressure, due to the presence of the solute. The rise predicted for a 1·0N of a crystalloid such as sugar, according to the familiar van 't Hoff formula, RT^2/s, is 0·483° at 90° C. Since the latent heat of vaporisation of water is greater at lower temperatures, and T is less, this rise is slightly less than the rise of 0·5010° expected in the ordinary Beckmann method at 100°. The values of the constant at lower temperatures are as follows: at 70° C, 0·414°; at 45° C, 0·353°; at 25° C, 0·303°; at 20° C, 0·291°.

Reverting to the experimental procedure, the following device was found to be essential for accurate readings. The silver tube was kept highly polished, but as it was very difficult to detect the first trace of dimming, a portion of the tube was so treated that no dew deposited on it, and thus a contrast between polished and slightly dimmed surface was obtained. The test of dew formation or disappearance was the formation of a sharp boundary or its vanishing point. To produce this effect boiling water was run through the silver tube and the bottom corner of the tube was dipped once into boiling conductivity water. The water evaporated, but thereafter no dew would form on this part of the surface. In this way the boundary line in a dew-point experiment ran diagonally across the lowest part of the side of the tube. The next step is to pass practically boiling water through the prepared silver tube and insert the latter into the glass vessel to about 1 cm. above the surface of the soap solution. This prevents (*a*) condensing large amounts of water on the silver tube, (*b*) altering the surface of the silver, (*c*) dimming the glass when heavy dew is evaporated, (*d*) changing the concentration of the solution. The whole apparatus with the hot water passing through it is then inserted into the transparent thermostat, as in Fig. 50 (*a*). The glass tap is kept open for a few minutes to equalise pressure outside and inside, since the vapour pressure of the solution is considerable at 90°, which is the temperature to which the transparent thermostat is adjusted. The tap is then closed.

The determination is now begun by very gradually lowering the temperature of the water running through the silver tube, noting the the thermometer contained in it and also the thermometer in the thermostat with its bulb close to the solution tube. On the first sign of dew formation the two thermometers are read. Immediately the supply of heat to the adjustable thermostat, which furnishes the water for heating or cooling the silver tube, is increased so as to raise slowly the temperature of the running water. The dew disappears and the two thermometers are again noted. Appearance and disappearance of dew are thus made use of.

McBain claims that the results are as accurate as an ordinary Beckmann determination in *dilute* solution, and of course the method has special advantages for soap solution determinations for the reasons already mentioned. For *moderate* concentrations of ordinary electrolytes the method is more accurate than the Beckmann method. Thus, from the data given in Landolt and Börnstein's tables, the dissociations indicated for normal solutions of KCl and NaCl are 80 per cent. and 94 per cent. respectively, whereas the dew-point method gives 78 per cent. and 76 per cent. respectively, in agreement with the results obtained by the same method for the corresponding acetates, namely, 78 and 74 per cent.

Experimental Results and Deductions from them.

In Concentrated *Soap Solutions the only Crystalloidal or Electrolytic Constituent is the Potassium or Sodium Ion.*—This means that nearly half of the current is carried by the negative colloid, which must be as good a conductor as an ordinary ion. To take a single case, the dew-point method shows that a 1 normal solution of potassium stearate exhibits a rise of boiling point of 0·20° at 90° C.; hence the total concentration of all ions and molecules is 0·42N. This solution has, at 90°, an equivalent conductivity of 113·4 reciprocal ohms, that of 1 normal potassium acetate being 176·9 at the same temperature. It is evident that at this concentration the stearate conducts about two-thirds as well as the acetate, and must, therefore, be regarded as a good conductor.

We have now to consider the concentration of the metallic ion present. If the negative ion were an ion at all the high molecular weight of the stearate radicle would lead us to predict that the stearate ion would not conduct as well as the acetate ion (116 recip. ohms at 90°). The mobility of the stearate ion might, in fact, be about 90 reciprocal ohms. This, with a mobility of 188 reciprocal ohms for the potassium ion, would make the conductivity of potassium stearate 278 when dissociation is complete. Using this result, the concentration of the potassium ion is given by $\frac{113}{278} \times 1{\cdot}0\text{N} = 0{\cdot}41\text{N}$. This equals the total observed concentration of crystalloidal constituents, 0·42N, within the experimental error as given by the dew point. Hence everything

else, that is the whole of the stearate including whatever carries the equivalent of this large amount of electricity, must be colloid and not simple unpolymerised stearate. Salmon (*Trans. Chem. Soc.*, **117**, 530 (1920)) has made a series of determinations of the potassium and sodium ions concentration or more strictly speaking their activities in potassium and sodium soap solutions respectively, and also in gels by means of e.m.f. measurements; the numerical values agree satisfactorily with those calculated by McBain.

The Concept of Highly Mobile Ionic Micelles.—Bayliss (*Proc. Roy. Soc.*, **B**, **84**, 229 (1911)), dealing with the osmotic pressure of Congo red solutions, makes several alternative suggestions, among which occurs "the possibility of aggregated simple ions carrying the sum of the charges of their components". Independently, McBain, in 1913, put forward the conception of a highly mobile heavily hydrated micelle in order to remove some of the difficulties in interpreting the properties of acid and alkali albumens, since it reconciles their enormous viscosity with their good electrical conductivity. McBain has developed this idea to a large extent in connection with soap solutions as has already been pointed out.

According to Stokes' law for a sphere of radius r moving through a liquid of viscosity η the velocity v of the body is given by $v = F/6\pi r\eta$, where F is the force causing the motion. It is known, in view of the work of Perrin and others, that this expression applies to particles of colloidal dimensions. In conductivity experiments the force is due to the electric charge upon the particle. If this charge could be varied without other alteration of the ion, the mobility or conductivity would vary in direct proportion to the driving force. If, on the other hand, a number of ions, say a dozen, were to coalesce, the resulting particles would be driven by a force of 12F. The velocity would not be proportionally so great, for the radius of the sphere would now be increased by $r\sqrt[3]{12} = 2{\cdot}3r$. The new velocity would be $12/2{\cdot}3 = 5{\cdot}2v$. This five-fold increase in mobility of the aggregate would, in practice, be counterbalanced by its greatly enhanced electrostatic potential in attracting water molecules and other material, so that such an aggregate would become a *heavily hydrated* micelle. The result would be a colloidal particle of about the same mobility as a rather slow true ion. The hydration would account for the enormous mechanical viscosity observed in all the systems mentioned, and also the fact that it varies with the concentration of other constituents.

In Dilute *Soap Solutions the Colloid Breaks up into Simple Ions and Simple Undissociated Soap Molecules.*—With the dew-point method 0·2N solutions were the most dilute which could be accurately dealt with. With potassium palmitate solutions of this concentration at 90° the results were as follows: Lowering of dew point = rise of boiling point = 0·12°. Hence total concentrations of all ions and molecules present = 0·25N. The molar conductivity of 0·2N potassium palmitate at 90° is 111 reciprocal ohms. If the conductivity at infinite dilution is 304, the concentration of potassium ions is 0·072N; if it be 278, the

concentration is 0·080N. Hydrolysis does not affect this result by more than about 2 per cent., and this may be neglected for our present purpose.

Taking the second result, concentration of potassium ions = 0·080N, the concentration of total crystalloids being 0·25N, leaves a concentration of (0·25 − 0·08), or 0·17N for crystalloids other than the K^+. The total undissociated soap is 0·200 − 0·080 = 0·120N. Thus, even if all the undissociated soap is in simple crystalloidal form, there is still a 0·17 − 0·12 = 0·05N concentration of crystalloid to be accounted for, and this must be afforded by simple palmitate ions, since the hydroxyl ions have been shown to be only about 0·001N. The small balance of 0·03, namely the difference between the K^+ (0·08N) and the simple palmitate ions 0·05N, is all that can be colloid. Not more than one-fourth of the undissociated palmitate nor more than three-eighths of the palmitate ion can be in the colloidal form. If there be some of each in the colloidal form this has to be divided up between them so as not to exceed a total of 0·03N.

It is evident that in 0·2N soap solution the break down of colloid has proceeded fairly far, and further dilution would complete it. We thus have a clear case of transition from colloidal to crystalloidal state depending upon the concentration. The transition is reversible.

Molecular Weights of Typical Solutions of Sodium Salts of Fatty Acids at 90 °C.

McBain and his collaborators have investigated by the dew-point method a great number of such cases involving potassium as well as sodium salts. For purposes of illustration only the sodium salts are referred to here. The rise in boiling point of these salts as a function of concentration is shown in the following table. It will be observed that the data cover simple non-colloidal substances such as the acetate right up to the behenate.

TABLE I.—RISE OF BOILING POINT AT 90° C. FOR SODIUM SALTS.

Weight Normality.	Behenate C_{22}.	Stearate C_{18}.	Palmitate C_{16}.	Myristate C_{14}.	Laurate C_{12}.	Caprylate C_8.	Acetate C_2.	Any Non-Electrolyte.
0·2	0·09	0·11	0·13	0·14	0·15	0·17	—	0·10
0·5	0·11	0·18	0·20	0·24	0·28	0·37	0·45	0·24
0·75	—	0·22	0·24	0·28	0·32	0·50	—	0·36
1·0	0·09	0·23	0·25	0·29	0·34	0·62	0·84	0·48
1·5	—	0·18	0·22	0·27	0·33	—	—	0·72
2·0	0·11	0·19	0·50	—	—	—	—	0·97
3·0	—	0·30	1·23	—	—	—	—	1·45

TABLE II.—TOTAL CRYSTALLOIDAL MATTER (IONISED AND OTHERWISE; CALCULATED FROM DATA OF TABLE I.) IN SODIUM SALT SOLUTIONS AT 90° C. MOLES PER 1,000 GRAMS OF WATER.

Weight Normality.	Behenate.	Stearate.	Palmitate.	Myristate.	Laurate.	Caprylate.	Acetate.
0·2	0·19	0·23	0·27	0·29	0·33	0·35	—
0·5	0·23	0·37	0·41	0·50	0·58	0·77	0·93
0·75	—	0·46	0·50	0·58	0·66	1·04	—
1·0	0·19	0·48	0·52	0·60	0·70	1·28	1·74
1·5	—	0·37	0·46	0·56	0·68	—	—
2·0	0·23	0·39	1·04	—	—	—	—
3·0	—	0·62	2·55	—	—	—	—

The results given in the two tables show certain interesting characteristics. It is evident that the salts fall into two classes. From the acetate up to the caprate C_{10} the behaviour is regular, showing dissociation. On the other hand, from the laurate upwards the curve representing rise of boiling point (or calculated solute content) passes through a pronounced maximum at about 1 normal, and a minimum at 1·5 normal. Above this concentration the rise of boiling point or lowering of vapour pressure rapidly increases again.

It may be mentioned that the stearate above 1·5 normal is hardly a solution; 1·5N sodium stearate at 90° is a viscid gum. On the other hand, 2·0N potassium laurate solution with a similarly shaped curve is a clear oily liquid. The form of the curve is thus due to the constituents in the system and is not due to mechanical effects, *e.g.* gel formation, skins on the surface, or other changes of state. The effect is also not due to hysterisis, as is the case in the dehydration of certain gels, for it is independent of the age or method of preparation of the soap solution or whether water may have been previously added or taken away. It will be pointed out later that the existence of the minimum in the boiling point rise is due to dehydration of the colloidal constituents, thereby releasing a quantity of solvent which effectively dilutes the solution and thus produces a diminished rise in the boiling point. Were it not for this, the boiling point would rise steadily all the way with increase in concentration.

In 1·0N *Solutions at* 90° *the total Colloid present equals at least* 15 *per cent. in the case of Hexoate, increasing to nearly the whole in the case of the Higher Soaps, but falling off rapidly with Dilution.*—In the preceding table have been given the concentrations of the total crystalloidal matter in any one of these solutions, namely, the sodium ion, the simple soap ion, such as the palmitate ion P, and the simple undissociated soap molecules, such as NaP. McBain next proceeds to calculate the concentration of the metallic ions, say the sodium ions, by conductivity measurements. For the moment we assume that the ion activities and ionic concentrations are sensibly identical. To calculate the concentration of sodium ion in any solution the values taken for the mobilities of the negative radicles are: behenate to laurate, 90; caprate, 92; caprylate, 94; caproate, 98; acetate, 116;

and for sodium, 139. The results of the calculation are given in the following table:—

TABLE III.—CONCENTRATIONS OF SODIUM IONS IN SALTS AT 90° C.

Weight Normality.	Stearate.	Palmitate.	Myristate.	Laurate.	Acetate.
0·2	0·053	0·079	0·085	0·099	0·140
0·5	0·166	0·195	0·216	0·239	0·303
0·75	0·272	0·286	0·324	0·350	0·409
1·0	0·386	0·369	0·405	0·455	0·511
1·5	0·553	0·553	0·543	0·615	0·664

By subtracting the corresponding values of Table III. from those of Table II., we arrive at the values of crystalloidal constituents other than the sodium ions. That is we obtain the values of the simple soap anions together with the simple undissociated soap molecules where such exist. These are given in the following table:—

TABLE IV.—CONCENTRATIONS OF CRYSTALLOID CONSTITUENTS OTHER THAN SODIUM IONS AT 90° C.

Weight Normality.	Stearate.	Palmitate.	Myristate.	Laurate.	Acetate.
0·2	0·18	0·19	0·20	0·23	—
0·5	0·20	0·22	0·28	0·34	0·63
0·75	0·18	0·21	0·26	0·31	—
1·0	0·09	0·15	0·20	0·25	1·23
1·5	− 0·20	− 0·11	0·02	0·07	—

The data given in the above table represent simple organic ion and simple molecule of the undissociated soap. By subtracting these values from the apparent normality of the solution as given in the first column, we obtain a quantity which must represent the colloidal part of the soap. This colloid of course includes ionic micelle and colloidal undissociated soap aggregate. The values are given in the following table:—

TABLE V.—CONCENTRATIONS OF TOTAL COLLOID IN SODIUM SALT SOLUTIONS AT 90° C.

Weight Normality.	Stearate.	Palmitate.	Myristate.	Laurate.	Acetate.
0·2	0·02	0·01	0·00	− 0·03	—
0·5	0·30	0·28	0·22	+ 0·16	− 0·13
0·75	0·57	0·54	0·49	0·44	—
1·0	0·91	0·85	0·80	0·75	− 0·23
1·5	(1·70)	(1·61)	1·48	1·43	—

It is necessary to consider the validity of this comparison of osmotic with conductivity data. It is undoubtedly the case that the osmotic

values are too high, presumably, as already mentioned on account of the hydration of the solute. Thus the dissociation deduced for sodium acetate from conductivity is less than the osmotic activity by 20 to 23 per cent. Were all this due to hydration, 7 or 8 moles of water would have to be combined with the acetate and its ions, a not improbable result. On the other hand McBain concludes that the results of conductivity measurements are too low, on account of the retarding influence due to viscosity. It is unknown what the exact viscosity correction should be in such cases where the colloid content is large, and the system consequently heterogeneous. McBain considers that the correction for viscosity is not a large one, in spite of the actual great viscosity which is due to aggregates floating in a dilute solution of an electrolyte, and we know from Lodge's original determinations of mobility of ions in a set jelly (where the mechanical viscosity is enormous) that the mobility is very little less than that in pure water. In the case of the acetates the viscosities of normal solutions at 18° C. exceed that of water by 26 per cent. Although this would be somewhat less at 90° C. it is ample to account for the divergence between conductivity and osmotic effect, but probably both viscosity and hydration contribute their share. It may be pointed out that the divergence between the two different kinds of measurement, conductivity and osmotic effect, in the case considered is in the opposite sense to that considered in (Chap. VIII.) dealing with strong electrolytes, in which it was found that the activity of the ions, as shown by the osmotic effect, is less than their concentration as shown by conductivity. In the present case the osmotic activity observed is certainly too great and the conductivity results too small, for the reasons cited. And yet in concentrated solutions of the higher soaps the osmotic effect is not enough even for the sodium and potassium ions alone as deduced from conductivity; compare the results for sodium stearate and palmitate at 1·5N in Tables II. and III. which lead to negative and therefore impossible values in these cases in Table IV. Referring to Table V. it will be seen that in the case of sodium stearate and palmitate, and also in the case of potassium laurate, the colloid content is greater than it could possibly be. Here the correction just discussed would operate in the wrong direction. The obvious course is to admit that the basis of calculation of the concentration of sodium ions in concentrated solutions is incorrect, in that the ionic micelle has a mobility even higher than the assumed value, *viz.* 90 reciprocal ohms at 90° C. To reconcile the data for 1·5N sodium stearate it is necessary to assume for the micelle a mobility at least as great as that of the potassium ion, 188 reciprocal ohms. This could be effected by diminishing hydration, giving the micelle a mobility which varied continuously and considerably with concentration.

Passing to the normal solutions the point to notice is that from caprate upwards these solutions contain colloid. In caprate only 15 per cent. is present in that form, whilst in stearate 91 per cent. is colloid. In every case the amount of colloid falls off steadily with decrease in concentration.

What has been established so far, as recorded in the tables already given, is the approximate total amounts of colloid and crystalloids present. The next problem is to allot these totals amongst the various crystalloid and colloid entities, namely, metallic ion, simple anion, undissociated simple molecules of the salt, micelle, and undissociated neutral colloid. A preliminary attempt to solve this complex problem has been made by McBain on the basis of certain assumptions. No details need be given in this place. It is evident that further investigation will eventually solve the matter in a definitive form. It may be mentioned, however, that at the present time it appears reasonable to divide up the total available colloid (Table V.) between neutral undissociated colloid and ionic micelle on the basis that 1·5 moles of undissociated soap are agglomerated for every mole of fatty acid that is agglomerated.

Composition of the Ionic Micelle.—This is likewise a problem which is not completely solved. The simplest view would be to consider the micelle as an agglomeration of, say, palmitate ions, heavily hydrated, thus—

$$(P)_n^{n(-)} . mH_2O \quad . \quad . \quad . \quad . \quad (1)$$

A more probable formulation would allow for the likelihood that some of the undissociated soap is adsorbed or united with the palmitate ions to form a micelle having the structure—

$$(NaP)_x . (P)_n^{n(-)} . (H_2O)_m \quad . \quad . \quad . \quad (2)$$

These formulas can only represent a general scheme for the micelle. Their composition must alter continuously with the concentration or upon addition of salts. Thus, in very concentrated solutions or in presence of large amounts of another electrolyte, such as sodium hydroxide, the soap must be nearly all neutral colloid having the composition—

$$xNaP . mH_2O \quad . \quad . \quad . \quad . \quad (3)$$

The question left open is as to whether in moderate concentrations the micelle has the formula (2) or the formula (1). On formula (2) the micelle alters gradually from (2) to (3) as the dissociation is driven back; on the other alternative, formula (1), driving back the dissociation does not alter the composition of the micelle (except by dehydrating it somewhat), but, of course, alters its number and leads to the production of neutral colloid. It is always to be remembered that, in dilute solution, neutral, crystalloidal, undissociated soap does exist independently.

As regards the number of charges on any single micelle, McBain considers that these must be at least 10, so that the molecular weight of a micelle is at least 3,000, since the single palmitic gram-ion has a weight of 255.

Prior to the introduction of the micelle idea, the colloidal constituent in soap solutions and in analogous cases was considered to be chiefly undissociated agglomerated soap molecules with adsorbed hydroxyl ion giving the individual a net negative charge. The metallic ions present formed the outer layer of the electrical "double layer," and the

magnitude of the charge depended upon the facility of slip, already discussed in the chapter on colloids in Vol. I. So far as is known there are many cases in which the charge exhibited by a colloid has this origin. In applying it to the soaps it is evident that we would have to assume large hydrolysis of the soap, so as to furnish sufficient hydroxyl ions, which, by being adsorbed in sufficient quantity, will confer the necessary mobility upon the colloid individual to account for the conductivity. This would involve in turn the production of a considerable amount of free undissociated palmitic acid, even though the *free* hydroxyl ions were small in number. McBain has shown, however, that palmitic acid cannot exist in the free state in the presence of even the low concentrations of alkali characteristic of these solutions. This view must therefore be abandoned, and in fact McBain substitutes the micelle theory in its place.

The Influence of Concentration upon the Composition of the Micelle explains the Anomalous Conductivity Curves of Soap Solutions.—The assumption already made is that in dilute solution the micelle has the composition $(P)_n^{n(-)} . mH_2O$, which gradually alters mainly, though not entirely, to the non-conducting form at very high concentration, this form being represented by $xNaP . yH_2O$. This transition takes place *via* the intermediate form $(NaP)_x(P)_n^{n(-)} . mH_2O$. As regards the conductivity results, it has been definitely established that the higher soaps in solution, quite apart from the small amount of free alkali present, exhibit minimum conductivity in 0·1 or 0·2N solutions. In higher concentrations the conductivity rises appreciably up to 0·5N or N solutions where a maximum is observed. This is direct evidence that the ionic micelle is a better conductor than the simple anion which it replaces. The ultimate falling off in very concentrated solutions is due to the diminishing dissociation of the salt as a whole.

It has already been mentioned that the rise in boiling point or lowering in vapour pressure passes through a local maximum at 1·0N. Diminishing hydration and diminishing dissociation of the colloidal electrolyte combine to reduce the lowering effect, and it therefore falls to the local minimum observed at 1·5N. There must be a limit to this action as the proportion of total water present gets less, hence the rise on boiling point or diminution in vapour pressure tends to increase with increase in concentration beyond 1·5N.

The diminishing hydration is not due to water becoming scarce, for the fact that the vapour pressure of a 1·5N solution is greater than that of a 1·0N solution means that the water is more available in the 1·5N case. The hydration being less in 1·5N solution, where the water is very active and available, can only be explained by alteration in the formula of the micelle such as is represented by an increasing proportion of undissociated soap in it. A further argument for this is afforded by the divergence in behaviour between the potassium and sodium soaps. This cannot be readily explained if the micelle in each is the same, as it would be if formula (1) were correct at all concentrations. But if the micelle is represented by formula (2) it will contain potassium

soap molecules in one case and sodium soap molecules in the other, so that a difference in behaviour is not improbable. The nature of the divergence referred to is that the potassium soaps are more colloidal than sodium soaps at the same concentration.

Ammonium Soaps, so far as they have been Studied, agree with the Conception here presented.—These soaps were first investigated by F. Goldschmidt and Weissmann in 1913 (*Kolloid-Zeitsch.*), as well as by McBain and his collaborators. Like the sodium soaps they exhibit fairly high conductivity, which in this case cannot be due possibly to products of hydrolysis, for ammonia is a feeble electrolyte. All these solutions are appreciably hydrolysed as is shown by the increase in conductivity caused by addition of excess of ammonia, though it is a poor conductor. These results can be interpreted as showing that the simple fatty ion existing in more dilute solutions is being replaced in stronger solutions by an ionic micelle which is a better conductor.

In Mixture of Soaps the tendency is to form more Micelle. Addition of Electrolytes exert Opposing Influences, first by their Dehydrating Effect, secondly by the fact that they drive back the Dissociation, if there is an Ion in common.—By dehydration the speed of the micelle is increased, and with it the conductivity. The driving back of the dissociation of the soap, which also accompanies dehydration tends obviously to decrease the conductivity. There is also the possibility of a mixed ionic micelle being formed, containing both salts adsorbed or united. The driving back of dissociation, if carried far enough, gives rise to the familiar salting out effect.

At Low Temperature there is more Micelle and it is more Hydrated than at Higher Temperature.—From dew-point measurements it can be concluded that the apparent osmotic effect is relatively somewhat greater at lower temperatures, but this point requires more detailed investigation. In connection with electrical conductivity the very high temperature coefficient observed may be ascribed to diminution of hydration as the temperature increases. This is strongly supported by the great increase in viscosity with lowering of temperature which has been measured by F. Goldschmidt.

Dew-point Lowerings of Soap at Extreme Concentrations.—In Table I. the data for a number of sodium soaps were given over a moderate concentration range. In the following table are given the results of observations in the case of sodium palmitate up to extremely high concentrations at 90° C. :—

TABLE VI.

Weight Normality.	Moles H_2O to 1 NaP.	Lowering in °C.	Concentration of Crystalloid.
3·0	18·49	1·23	2·55
4·22	13·15	1·32	2·73
8·12	6·83	2·64	5·48
12·56	4·42	4·26	8·82
14·29	3·88	4·72	9·77

McBain points out that the values given in the last column have no precise significance. They serve to show, however, that the lowering finally becomes proportional to the weight normality. It will be observed that the lowering in vapour pressure or rise in boiling point increases steadily through all concentrations above 3N, that is, there is no further maximum or minimum met with such as was encountered at 1N and 1·5N.

The Behaviour of Typical Dyestuffs and Indicators may be Explained on the Micelle Basis.—It is obvious that any satisfactory theory of the behaviour of soap solutions should also be capable of including the analogous cases represented by dyes, indicators, and acid and alkali proteins. According to the micelle theory we would expect to find in all these cases pronounced electrical conductivity co-existing with deficient osmotic activity.

The work of Donnan and Harris, already discussed at some length in another connection—membrane equilibria—as well as the work of Bayliss (*loc. cit.*), shows that the osmotic pressure of Congo red is considerable, but does not exceed that of a simple non-electrolyte. On the other hand the conductivity is unexpectedly high, being nearly equal to that of sodium chloride. The existing data for other dyes and indicators are of a similar nature. Many of the peculiarities encountered in these cases, particularly in connection with the sometimes enormous effect of neutral salts are to be ascribed probably to a disturbance of the equilibria between colloid and crystalloid, and hence between the various possible crystalline forms of the indicator. Definite equilibria between crystalloid and colloid forms have been demonstrated in the case of the soaps.

As regards proteins, the data summarised by Pauli (*Trans. Faraday Soc.*, **9**, 54 (1913)) in connection with viscosity and electrochemical properties led him to infer a heavily hydrated polyvalent ion. One point of great interest has already been studied in connection with acid protein solutions, namely, the effect of concentration upon equilibria involving micelles. Manabe and Matula working with Pauli have re-examined electrometrically the combination of albumin with each ion of hydrochloric acid (*Biochem. Zeitsch.*, **52**, 369 (1913)). The maximum difference between the amounts of hydrogen and of chlorine ions taken up by 1 per cent. albumin occurs at about 0·02N HCl, thereby showing maximum formation of ionised salt. This maximum coincides with maximum viscosity and maximum osmotic effect, as measured by an osmometer. Further addition of HCl drives back the ionisation with extreme rapidity. This very great influence of concentration of HCl is to be expected on the basis of mass action. Thus, in the equilibrium between albumin and its ions, suppose, for example, that the micelle is decavalent, then, denoting the albumin radicle by A and neglecting hydration, the equilibrium can be represented by—

$$H_{10}A^{10+} + 10Cl^- \rightleftharpoons AH_{10}Cl_{10}.$$

In this case the ionisation would depend upon the tenth power of the chlorine ion concentration, so that doubling the concentration of HCl

might produce the effect found by Pauli. Were the case of the soap micelle exactly similar, then doubling the concentration of say 0·5N sodium palmitate solution should have an extremely great effect on the dissociation of the electrolytic colloid. This, however, is not observed (*cf.* Table III.). There must be some compensating factor, and McBain suggests that this is to be found in the gradual alteration in the composition of the palmitate micelle (*i.e.* its degree of hydration and more especially its $(NaP)^x/P_n^-$ ratio) as the concentration increases, already inferred on other grounds. It is assumed that the dissociation constant of the soap is likewise greatly altered concomitantly, and hence the extent of dissociation is not largely affected. This conclusion obviously requires further experimental confirmation.

In conclusion it may be mentioned that Pauli (*Kolloid-Zeitsch.*, **21**, 49 (1917)) has applied the micelle theory to the case of colloidal ferric hydroxide, regarding this colloid as consisting of a moderately dissociated colloidal electrolyte with chlorine ion as the anion and an ionic micelle as the cation.

CHAPTER XII.

Systems not in equilibrium studied from the thermodynamic standpoint—Affinity and its measurement by means of vapour pressure, solubility, and electromotive force—Oxidation and reduction processes—Change of affinity with temperature.

Chemical Affinity.

We now pass on to the question of chemical affinity and its measurement. The conception of some kind of attractive force or affinity between portions of matter is one of the oldest in science, but until recently it never got beyond the stage of obscure definition. It evaded quantitative measurements, although attempts were made in this direction by Berzelius, Mitscherlich, Wilhelmy, Guldberg, and Waage. What at first sight appears to be the most promising definition, namely, that the *speed* of reaction gives a measure of the affinity, cannot be retained when we remember how dependent reaction velocity is on a variety of circumstances, quite unconnected with the process itself, *e.g.* the presence of catalysts. The first successful solution of the problem is due to Helmholtz, but Helmholtz did not pursue it. It was really rediscovered by van 't Hoff in 1883, who came to the conclusion THAT THE ONLY TRUE MEASURE OF CHEMICAL AFFINITY BETWEEN SUBSTANCES WHICH MANIFESTS ITSELF BY CHEMICAL REACTION WHEN THE SUBSTANCES ARE BROUGHT INTO CONTACT IS GIVEN BY THE MAXIMUM EXTERNAL WORK AT CONSTANT TEMPERATURE AND AT CONSTANT OR PRACTICALLY CONSTANT VOLUME WHICH IS DONE BY THE SYSTEM IN PASSING FROM THE INITIAL STATE TO THE STATE FINALLY REACHED BY THE REACTION, *i.e.* THE EQUILIBRIUM POINT. Note, for reactions which involve a volume change we subtract or add the work term involved by this change, and what remains is the affinity. To take a simple physical illustration of a "reaction" which involves practically no volume change. Suppose two

Affinity (Historical Note).—The measure of affinity, say, of a solution for the solvent being given quantitatively by the change in free energy involved in the transfer of unit mass (say 1 mole) of solvent from one to the other, this being calculable for the reversible case, by the vapour pressures according to the equation

$$\frac{\partial F}{\partial m} = \int_{p}^{p} v dp,$$

was first given by Helmholtz (see two papers, *Sitzungsberichte der Akademie der Wissenschaft zu Berlin*, 1882). In his own words "$-\frac{\partial F}{\partial m}$ is to be distinguished as the force with which the water of the solution is attracted".

vessels containing aqueous solutions of salt at two different concentrations c_1 and c_2 ($c_1 > c_2$) are brought into contact. Will any diffusion occur? On van 't Hoff's idea we would say yes, provided external work can be done by the system in the process. Evidently, if we transport 1 mole of salt from the greater concentration to the less, positive work will be done by the system amounting in the most favourable case, *i.e.* as a maximum limit, to the expression—

$$RT \log \frac{c_1}{c_2} \text{ per mole diffused.}$$

Hence we would expect the change to be a diffusion from strong to weak, where $c_1 > c_2$, and such is, of course, the actual case. Further, the above expression shows that when $c_1 = c_2$ there is no nett work gained or lost by transferring 1 mole from one vessel to the other at constant temperature. But this is a definition of the equilibrium point, and hence equilibrium should be reached when the concentrations are identical. Such is actually the case. It will thus be seen, how, in this example, van 't Hoff's idea of maximum work as a measure of affinity or tendency to react fits the facts well. It might be pointed out (for reasons to be given shortly) that practically no heat effects take place in the above case. Van 't Hoff's view as to the real cause of a reaction was not universally accepted at first.

As long ago as 1854 another view, and at first sight a plausible one, had been put forward by Thomsen, and later, in 1867, was supported by Marcelin Berthelot, who considered the heat effect as being the determining factor. This is known curiously as the principle of maximum work. This principle was a very simple one, since it stated merely that the heat which is *developed* by a chemical change indicates the direction in which a change will proceed; when the possibility of evolution of heat exists, then the reaction will proceed in such a direction as to bring this about. Take, for example, hydrogen and oxygen gas. Two grams of the former with 16 grams of the latter will develop 69,000 calories, when uniting to form water. The principle just referred to sees in this heat development the cause of the formation of the water, which as we know takes place when the mixture of the two gases is ignited. Conversely, if we consider nitrogen and chlorine we find that by their union no heat is developed; on the contrary heat is absorbed. So here, instead of the union of the elements, the tendency is towards the decomposition of the compound. When the union has been achieved by indirect means the decomposition can be brought about by the slightest shock. For many years this was a fundamental principle of thermochemistry, and many facts were known to support it. In spite of this it is not difficult to furnish examples of cases in which chemical changes take place with the absorption of heat.[1] Freezing mixtures, like that of

[1] The lack of the validity of the Thomsen-Berthelot principle is shown when one applies thermodynamics to chemical problems. Horstman, 1869 (Ostwald's *Klassiker*), was the first to show the way of applying these thermodynamical principles. A few years later Lord Rayleigh (*Proc. Roy. Inst.*, 7, 386, 1875) questioned

hydrochloric acid and Glauber's salt, whose operation depends on the accomplishment of a chemical reaction thus—

$$Na_2SO_4 10H_2O + HCl \rightarrow 2NaCl + 10H_2O + H_2SO_4$$

really contradict the principle of Berthelot. Further, the majority of reactions proceed only to a certain limit, this being true of all reactions in homogeneous systems (gas or solution). Thus let us bring equivalent quantities of gaseous hydrochloric acid and ammonia into a given space; a part of the gases will unite to form solid ammonium chloride, and the production of this salt will extend to the point corresponding to its dissociation pressure at the given temperature. On the other hand, let us bring "solid" ammonium chloride into a given space at the same temperature; dissociation takes place, *i.e.* the substance which was formed in the first case is decomposed in the second. But in the first case we are dealing with an exothermic reaction; in the second case with an endothermic one. Berthelot's principle postulates the existence of exothermic reactions only. In general, therefore, every single instance of reversible reaction is sufficient to disprove the universal validity of Berthelot's principle. Further instances may be cited. Suppose we have ice and water in contact with one another at 0° C., we know that there is no tendency for either to increase at the expense of the other, *i.e.* they are in equilibrium. The experimental fact that at the equilibrium point their vapour pressures are identical is thus in agreement with the van 't Hoff definition of affinity. On the other hand, a very large heat effect, *i.e.* an evolution of 80 calories per gram, occurs on solidifying the water, and if Berthelot's principle held good we would naturally expect the system to change into the solid state completely. Also with reference to the diffusion experiment in the case of two solutions of salt at different concentrations—the heat effect is immeasurably small, but the "reaction" takes place all the same. Here again the heat effect is no measure of the affinity. On the other hand, the vapour pressures being different (or the osmotic pressures which are related to the vapour pressures thus, $p_0 - p = \frac{\sigma}{\rho}P$) would lead one on van 't Hoff's view to predict a diffusion from the stronger to the weaker solution. The accomplishment of work and the development of heat in a chemical change do not mean therefore the same thing. They often go hand in hand as in the case of explosives, like gunpowder and dynamite. A compound like phosphonium chloride (PH_4Cl) solid, however, tends to decompose at ordinary temperatures into gaseous PH_3 and HCl with a marked absorption of heat. Yet the decomposition products of this compound may exercise a pressure of some twenty atmospheres. "Here we have a case where the possibility of accomplishing work does not coincide with the capacity to develop heat, and yet where it is obviously the capacity to do work which controls the direction of the change"

the validity of the Thomsen-Berthelot principle in a short paper "on the dissipation of energy". Rayleigh's views were further emphasised and extended to electrical systems by Helmholtz in 1882.

(van 't Hoff). The expression "maximum work" was, however, fortunately chosen by Berthelot, since the correct principle for the prediction of a reaction must connect the possibility of the change with the possibility of a concomitant accomplishment of work. In order to ascertain the change of free energy or the amount of external work done, which is associated with a chemical reaction, we must cause the reaction to occur isothermally and reversibly; and thereby we can obtain directly the desired information respecting the amount of maximum external work which can be obtained from the chemical change. Let us suppose that under the conditions described, the change may occur in any one of several ways; even then the change in free energy would always be the same. For otherwise we could complete the change in *one* way, and then we could come back by the other, and thus we could establish a reversible *isothermal* cyclic process by means of which any arbitrary amount of external work could be performed at the cost of the heat of the environment. But this is perpetual motion, and contrary to the Second Law of Thermodynamics, and thus we obtain the theorem :—

The change of the free energy of a chemical process is independent of the way in which the change is completed as long as it is reversible, and is determined solely by the initial and final states of the system.

We are thus at liberty to make measurements of work by quite different methods applicable to different cases, and consider the results as comparable, provided only that each single process be a reversible isothermal one. We have already seen that for practical purposes there are two methods of measuring external work which are in frequent use: (1) from vapour pressure determinations or the equivalent osmotic pressure in the case of solutions, using the three-stage work term $\int_2^1 vdp$ per gram-mole transferred, and (2) electromotive force measurements.

Let us take an example of how affinity can be measured by means of vapour pressure data. Well-known instances are the formation of hydrated copper sulphate, *i.e.* the affinity of copper sulphate for water; ferric chloride hydration; sulphuric acid and water. Let us take the latter case and suppose the question is: What is the affinity of water for concentrated sulphuric acid at the temperature T, given that p_0 is the vapour pressure over pure water and p_1 is the vapour pressure of water vapour over concentrated sulphuric acid?

The answer is that the affinity "A" of the water for the acid is $\int_{p_1}^{p_0} vdp$, and if the gas law is obeyed—

$$A = RT \log \frac{p_0}{p_1}.$$

One may note in passing that if we could get absolutely anhydrous sulphuric acid $p_1 = 0$ and $\log p_1 = -\infty$, or $A = +\infty$, *i.e.* the affinity

of the reaction would be infinitely great. As a matter of fact, such a state of things is unrealisable experimentally.[1]

Again take the case of the substances represented by $CuSO_4 x H_2O$. We know that below a certain temperature called the transition point $CuSO_4 . 5H_2O$ is a stable crystalline solid. Above a certain temperature it melts, giving a saturated aqueous solution of $CuSO_4 . 3H_2O$. We thus have the reaction—

$$CuSO_4 . 5H_2O \rightarrow \underline{CuSO_4 . 3H_2O + 2H_2O}.$$

Above the transition point the reaction occurs from left to right. There must therefore be a positive tendency or affinity in this direction, and hence in order to make the affinity term positive the vapour pressure of the water over the pentahydrate *above* its transition point must be greater than the vapour pressure of the water over the saturated trihydrate solution, and this has been experimentally verified. In general, when dealing with transitions from unstable to stable phases, the vapour pressure of a given compound over the *unstable* phase is always greater than its vapour pressure over the stable phase, this as a matter of fact being the cause of the change. Below the transition point, the vapour pressure of water on the saturated $[CuSO_4 . 3H_2O + 2H_2O]$ is greater than that over the crystalline pentahydrate and the direction of chemical change is reversed. Note that you must always in such instances of transition take into account the whole system on either side of the equation. In the simple case considered we were only dealing with the transfer of a single substance (say, water) from an initial to a final state, the reaction being carried out by this transfer. In general, however, we have to deal with the simultaneous reaction of two or more substances which give rise to new substances, *e.g.* $2H_2 + O_2 = 2H_2O$. In reactions which are characterised by the existence of an equilibrium point and an equilibrium constant, *i.e.* reactions occurring in gaseous mixtures or in solutions, the expression for the work of transforming certain amounts of the reactants (at a given temperature, pressure, or concentration) into resultants at the same temperature, but at another arbitrary pressure, or concentration, is evidently the van 't Hoff isotherm, *viz.*—

$$A = RT \log K - RT\Sigma\nu \log C.$$

If we are going to measure affinity by maximum work, we must therefore regard A as likewise representing the affinity of the process considered. The formula shows directly that when the arbitrarily chosen concentration terms occurring in the term $\Sigma\nu \log C$ are identical with the equilibrium concentration terms, $A = 0$, *i.e.* the affinity is zero as one would expect. In fact, the farther the arbitrary concentration terms are from the equilibrium values the greater is the value of A. This expression brings out conversely the extreme importance of the equilibrium

[1] The idea that the vapour pressure of a (pure) substance is a true measure of the "active mass" of the substance is due to Guldberg and Waage (1867). *Cf.* A. Pousot, *Comptes Rendus*, **130**, 829 (1900).

constant in the determination of affinity measurements. Note: An expression such as "the affinity of oxygen for hydrogen" by itself means nothing at all until we specify the concentration of the reactants and the concentration of the resultants which we are aiming at, and the temperature.

There is one special case to be noted. Suppose we start with substances at unit concentration and end with substances also at unit concentration (*i.e.* 1 mole of each per liter, which would hold equally for gases or solutions, or, say, at 1 atmosphere pressure of each, which would apply to gases only), then the arbitrary concentration terms are each unity, and since the log of unity is zero, the expression for the affinity becomes—

$$A = RT \log K.$$

The *thermodynamic* significance of the equilibrium constant is therefore this: Its logarithm is proportional to the maximum work involved in any given reaction in which we start with the reactants at unit concentration and end up with the resultants also at unit concentration.

Illustrations of the Measurement of Affinity by the Maximum Work produced by the Reaction. (*Cf.* Sackur's *Chemische Affinität und ihre Messung*, Die Wissenschaft Series.)

Let us first consider an instance of HOMOGENEOUS GASEOUS reactions. The affinity is given by the expression—

$$A = RT \log K - RT\Sigma\nu \log C.$$

Affinity must be specified with regard to the *number* of molecules of a given species taking part in the reaction. If we consider twice the number of molecules the affinity is doubled, and so on. Take as a special case the *affinity of hydrogen and iodine gases* for one another at a given temperature. If K is the equilibrium constant and $[H_2]$ $[I_2]$ represent the arbitrary concentration of the two substances in the initial state, and [HI] the final concentration of the hydriodic acid reached, then the affinity of the process $H_2 + I_2 \rightarrow 2HI$ per *mole* of hydrogen or iodine is—

$$A = RT \log K - RT \log \frac{[HI]^2}{[H_2][I_2]},$$

where

$$K = \frac{C^2_{eHI}}{C_{eH_2} \times C_{eI_2}}.$$

Suppose the initial arbitrarily chosen concentration of hydrogen and iodine is unity, and the concentration of the hydriodic acid is also to reach unity, then the affinity of the reaction under these conditions is simply—

$$A = RT \log K.$$

This case will now be illustrated.

A series of equilibrium constants at various temperatures have been calculated by Haber from Bodenstein's data and are given in Chap. III.

Vol. I. At 300° C. (573° abs.) the value of K which we require, namely $\frac{4(1-x)^2}{x^2}$, is $(8{\cdot}9)^2 = 80$ approx. The affinity per mole of hydrogen or iodine—

$$= \frac{2 \times 573}{0{\cdot}4343} \log_{10} 80 = +5000 \text{ calories approx.}$$

Again at the temperature 500° C. (773 abs.) K = 41 approx. Hence, under the particular conditions of concentration chosen, the affinity is given by—

$$A = \frac{2 \times 773}{0{\cdot}4343} \log_{10} 41 = +5760 \text{ calories.}$$

It is interesting to note that the *heat evolved* in the reaction is small, *viz.* 2800 calories approx. It is an example of where the Berthelot principle breaks down.

Another interesting case is *the affinity of oxygen for hydrogen.* Nernst and v. Wartenberg have shown that at 1000° abs. the degree of dissociation of water vapour at 1 atmosphere pressure is $3{\cdot}0 \times 10^{-5}$ per cent. That is, the fractional amount of 1 molecule of water dissociated according to the equation $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ is $3{\cdot}0 \times 10^{-7}$. There are therefore present in equilibrium at this temperature and pressure $3{\cdot}0 \times 10^{-7}$ moles of hydrogen and $\frac{3{\cdot}0}{2} \cdot 10^{-7}$ moles of oxygen for every mole of water (neglecting the actual decrease in water molecules, since the dissociation is so extremely small). For the equilibrium constant in terms of partial pressures (the equilibrium concentration being denoted by the suffix ϵ) we have therefore—

$$K = \frac{p^2_{\epsilon H_2} \times p_{\epsilon O_2}}{p^2_{\epsilon H_2O}} = \frac{9 \times 10^{-14} \times \frac{3}{2} \times 10^{-7}}{1} = 1{\cdot}35 \times 10^{-20}.$$

This is the dissociation constant of water vapour under the given conditions of temperature and pressure. The reaction we are considering is just the reverse of this, namely, $2H_2 + O_2 \rightarrow 2H_2O$, and we wish to find what the affinity of oxygen for hydrogen is, both being at 1 atmosphere pressure (in separate vessels) at 1000° abs., the reaction to take place so that the water vapour formed will finally be at 1 atmosphere pressure, also at 1000° abs. The expression per mole of oxygen is given by—

$$A = RT \log K' - RT\Sigma\nu \log p,$$

K′ being the reciprocal of K. We can thus write A in the form—

$$A = RT \log \frac{p^2_{\epsilon H_2O}}{p^2_{\epsilon H_2} \times p_{\epsilon O_2}} - RT \log \frac{p^2_{H_2O}}{p^2_{H_2} \times p_{O_2}}.$$

The arbitrarily chosen values denoted by p_{H_2}, p_{O_2}, p_{H_2O} have all been taken to be unity (at 1 atmosphere each), so that A reduces to

$$-\mathrm{RT}\log \mathrm{K} \text{ or } -\mathrm{RT}\log\frac{p^2_{\epsilon \mathrm{H_2}} \times p_{\epsilon \mathrm{O_2}}}{p^2_{\epsilon \mathrm{H_2O}}}.$$

That is, $\mathrm{A} = -1{\cdot}98 \times 1000 \times 2{\cdot}3 \log_{10} 1{\cdot}35 \times 10^{-20}$
$= +90{,}600$ calories.

This shows that there is a large positive affinity between hydrogen and oxygen gases when each is at 1 atmosphere pressure at the temperature 1000° abs.

The affinity of processes occurring in solution can be treated in a similar way. An interesting case is the affinity of the process of electrolytic dissociation in the case of weak electrolytes to which the Mass Law in the form of the Ostwald Dilution Law applies. If k is the dissociation constant of a weak electrolyte, then RT log k represents the work which would be necessary to cause complete breaking up of the molecules into ions in a *normal* solution. Since k has been shown by experiment to be always less than unity, it follows that the work is negative, *i.e.* the affinity of complete dissociation is negative, so that a normal solution of free ions is unstable, and combination to form undissociated molecules results. The "avidity" of a weak acid for a base we have already seen is put proportional to the dissociation constant k of the acid (Ostwald and Arrhenius). From the standpoint of the present discussion, it would be more correct to regard RT log k as the true measure of the avidity.

We can now pass on to the consideration of some typical heterogeneous reactions.

Application of the van't Hoff Isotherm to the Calculation of the Affinity between Substances in the Condensed State.

By the term condensed system is meant a system either in the liquid or solid state. Let us suppose that we have three separate vessels, the first containing liquid oxygen, the second liquid hydrogen, and the third, solid water (ice). The question is, what is the affinity of liquid oxygen and liquid hydrogen for one another, the reaction being so carried out as to yield ice at a given (low) temperature, T?

Above each of these liquid and solid forms there exists the corresponding saturated vapour. The pressure, or what is proportional to it, the concentration of each of these vapours, is a measure of the chemical activity of the corresponding condensed form in equilibrium with the saturated vapour. We can therefore regard the concentrations of the saturated vapours of oxygen and hydrogen as the arbitrary concentration values of the reactants from which the thermodynamic process starts. The concentration of the saturated vapour over the ice represents the arbitrary concentration value of the resultant at which the process ends. We have to calculate the affinity of the chemical process between these limits, for if we do this, the result will necessarily give the affinity of the reaction when carried out entirely in the condensed forms. This affinity is obviously given by the relation—

$$\mathrm{A} = \mathrm{RT}\log \mathrm{K} - \mathrm{RT}\Sigma\nu \log \mathrm{C},$$

where $\Sigma\nu$ log C refers to the concentrations of the *saturated* vapours of reactants and resultant, and K is the equilibrium constant of the reaction $2H_2 + O_2 = 2H_2O$, *in the entirely gaseous state.*

It is very important to realise that the affinity of the *condensed* substances is measured by an expression which involves the concentrations of the *saturated* vapours together with the equilibrium constant characteristic of the same reaction in the *gaseous* state. This conclusion depends upon the assumption that the pressure or concentration of a saturated vapour is a true measure of the reactivity of the condensed substance. The above expression is of great importance for it allows us to calculate the affinity of condensed reactions from measurements made upon the substances in the gaseous state. This point will be referred to again in discussing the application of Nernst's Heat Theorem to *gaseous* reactions.

Formation of Salts containing Water of Crystallisation.

The case which we shall consider is the affinity of *ice*[1] at 0° C. for various salts, some partially hydrated, others anhydrous (*cf.* Schottky, *Zeitsch. physik. Chem.*, **64**, 422, 1908). One mole of water is vaporised from the ice, its pressure altered to that in equilibrium with the salt, and then the vapour is imagined to be compressed into the salt. The process is simply the familiar three-stage distillation, the maximum work or affinity being—

$$A = RT \log \frac{p_0}{p_1}.$$

Assuming that the vapour obeys the gas laws, p_0 is the vapour pressure over ice, and p_1 is the pressure of water vapour in equilibrium with the salt. It has already been pointed out in the Phase Rule chapter, that in the case of dissociating salts such as $CuSO_4 . 5H_2O \rightarrow CuSO_4, 3H_2O + 2H_2O$, the dissociation pressure of the pentahydrate p_1 can be taken, as far as affinity is concerned, as likewise the equilibrium vapour pressure p_1 of the trihydrate, since both these salts are necessarily present to fix the equilibrium. Taking the above case as an example, therefore, the expression $RT \log \frac{p_0}{p_1}$ measures the affinity of ice for the trihydrate $CuSO_4 . 3H_2O$. A series of vapour pressure measurements, by means of the Bremer Frowein tensimeter for example, are therefore sufficient to allow one to calculate (say, in calories) the affinity of the reaction. At the same time it is interesting to compare the heat evolved or absorbed by the same reaction. Thomsen has carried out a long series of such measurements on the heat of the reaction between *liquid* water and various salts (see Thomsen's *Thermochemistry*, translated by Miss K. A. Burke. Ramsay series). In passing from ice to liquid water, 80 calories per gram, or 1440 calories per gram-mole are

[1] Strictly one cannot speak of the affinity of a substance but of the affinity of a process.

absorbed. It is necessary, therefore, to subtract 1440 calories from Thomsen's values to obtain the heat of reaction between ice and the corresponding salt. This has been done by Schottky, who has compiled a table which allows one to compare directly the affinity of the reaction with the heat evolved. Some of the data of Schottky's table are reproduced below. It will be observed that Q and A values though of the same order of magnitude are by no means identical. The greatest differences occur in the case of those substances quoted towards the end of the table. There is no doubt that these differences exist although it is to be remembered at the same time that the accuracy of measurement of the vapour pressures in some cases is not very great when the actual pressure is small. It is an interesting, though accidental relation that in all the cases quoted except two A is less than Q.

COLLECTION OF VALUES OF A AND Q FOR *ICE* AND ANHYDROUS OR HYDRATED SALTS.

(Schottky, *Zeitsch. physik. Chem.*, 64, 422, 1908.)

Reaction.	Q per Mole of Ice in Calories.	A per Mole of Ice in Calories.	Q − A.
$CuSO_4 3Aq + 2Aq$ . .	1190	840	350
$ZnSO_4 1Aq + 5Aq$ . .	554	480	74
$MnSO_4 1Aq + 4Aq$ . .	336	359	−23
$FeSO_4 6Aq + 1Aq$ . .	200	275	−75
$Na_2S_2O_3 + 5Aq$ . .	1056	962	94
$NaBr + 2Aq$ . . .	656	585	71
$BaCl_2 + 1Aq$ . . .	2010 (Schottky)	1410	160
$SrCl_2 2Aq + 4Aq$ . .	790	753	37
$NaC_2H_3O_2 + 3Aq$ . .	1284	907	377
$Na_2HPO_4 2Aq + 5Aq$.	640	424	216
$Na_2HPO_4 7Aq + 5Aq$.	640	280	360
$CuSO_4 1Aq + 2Aq$ . .	1645	1045	600
$Na_2HPO_4 + 2Aq$ . .	1410	860	550
$(COOH)_2 + 2Aq$ . .	1560	810	750
$BaCl_2 1Aq + 1Aq$ . .	2230	1060	1170
$ZnSO_4 6Aq + 1Aq$ . .	1810	450	1360
$MgSO_4 6Aq + 1Aq$ . .	2060	590	1470
$SrCl_2 + 2Aq$ . . .	2930	1430	1500
$CuSO_4 + 1Aq$ . .	4860	2350	2510
$MnSO_4 + 1Aq$ . .	3990	> 1130 (Difficult to measure owing to small p)	< 2860
$ZnSO_4 + 1Aq$ . .	6880	2350	4530

The Affinity of Carbon Dioxide (CO_2) *for Lime* (CaO).

The reaction is $CaO + CO_2 \rightarrow CaCO_3$.

Suppose we have a large reservoir of carbon dioxide at a pressure p_0 at a given temperature. Suppose that the dissociation pressure of

calcium carbonate, *i.e.* the pressure of carbon dioxide in equilibrium with lime and calcium carbonate at the same temperature, is p_1, the affinity of the reaction per mole is—

$$A = RT \log \frac{p_0}{p_1},^1$$

assuming that the carbon dioxide obeys the gas law. If the gas reservoir is at atmospheric pressure $p_0 = 1$, and $A = -RT \log p_1$. This is the affinity of carbon dioxide at atmospheric pressure, and at temperature T, for lime at the same temperature. Since p_1 is less than unity up to fairly high temperatures, this expression for A is a positive quantity. That is, if carbon dioxide at one atmosphere, and at ordinary temperatures, be brought into contact with lime, the affinity is positive, and the reaction resulting in the formation of calcium carbonate will proceed. If the temperature and pressure values are such that A is negative, this means that the affinity is negative, and therefore the reverse action will take place, namely, the dissociation of the carbonate.

Affinity of Oxygen for Metals.

One of the most important cases in which one wishes to measure the affinity is that of the oxidation of metals by oxygen gas. In general the reaction—

$$2Me + O_2 = 2MeO$$

does not go completely but reaches an equilibrium. The metallic oxide possesses a certain decomposition pressure at each given temperature, but this is small and extremely difficult to measure. The affinity of metal for oxygen *at any given pressure* can be determined by reducing

[1] The expression $A = RT \log \frac{p_0}{p_1}$ is, of course, only a special case of the van 't Hoff isotherm. The reaction considered is $CO_2 + CaO \rightarrow CaCO_3$. The equilibrium constant K at temperature T

$$= \frac{C_{\epsilon caco_3}}{C_{\epsilon co_2} \times C_{\epsilon cao}}$$

the term C_ϵ denoting the equilibrium concentration of the given substance *in the vapour state* (in contact with the solids). The term $C_{\epsilon co_2}$ corresponds to the partial pressure term p_1. We wish to find what the affinity of the reaction is (per mole of CO_2) when carbon dioxide at a pressure p_0 (corresponding to a concentration C_0) reacts with lime, the end products being in equilibrium, that is possessing the values $C_{\epsilon caco_3}$, $C_{\epsilon co_2}$, $C_{\epsilon cao}$. The term $RT\Sigma\nu \log C$ is thus $RT \log \frac{C_{\epsilon caco_3}}{C_{\epsilon cao} \times C_{0co_2}}$, and hence

$$A = RT \log \frac{C_{\epsilon caco_3}}{C_{\epsilon cao} \times C_{\epsilon co_2}} - RT \log \frac{C_{\epsilon caco_3}}{C_{\epsilon cao} \times C_{0co_2}} = RT \log \frac{C_{0co_2}}{C_{\epsilon co_2}}$$

$$= RT \log \frac{p_0}{p_1}.$$

The gas law is assumed throughout.

the oxide by means of a reducing agent whose affinity for oxygen is known. Thus, if we reduce the oxide by means of carbon—

$$MeO + C \rightarrow Me + CO \quad . \quad . \quad . \quad . \quad (1)$$

and then suppose this split up into—

$$MeO \rightarrow Me + \tfrac{1}{2}O_2 \quad . \quad . \quad . \quad . \quad (2)$$
$$\tfrac{1}{2}O_2 + C \rightarrow CO \quad . \quad . \quad . \quad . \quad (3)$$

By measuring the affinity in (1) and (3) we can calculate the affinity of (2) by subtraction. What we want is the *reverse* of equation (2). Let us take reaction (1), and suppose that at a temperature T the equilibrium is reached when CO has a pressure p_1. The first question is, will CO, at a pressure of 1 atmosphere, when brought into contact with Me, C, MeO, at the temperature T, cause a reduction or oxidation of the metal? Consider the vessel in Fig. 51. We can tell at once by measuring the work done in bringing 1 mole of CO from pressure 1 to pressure p_1.

The work A_1, *i.e.* the affinity of CO for Me, is $RT \log \frac{1}{p_1} = -RT \log p_1$. This is the reverse of equation (1).

$$\therefore -A_1 = \text{affinity of } [MeO + C].$$

Now if p_1 is less than 1 atmosphere, A_1 will be positive. We know from experience that if we bring in CO at 1 atmosphere pressure there is too great a concentration of the gas for equilibrium to be reached, and in accordance with the law of mass action some of the carbon monoxide must disappear so as to reduce its pressure. It disappears by reacting with the metal, giving oxide and carbon, that is to say an oxidation takes place. If, however, p_1 were greater than 1 atmosphere, then, if we were to change the gas pressure from p_1 to 1 atmosphere, we would find that the system would tend to produce more carbon monoxide to bring its pressure up to the equilibrium pressure p_1. That is to say, a reduction of the metallic oxide would take place. This brings out clearly how very careful one must be in saying that such and such a substance is a reducing agent. Whether it is a reducer or not depends on the conditions of the experiment. The above expression, that is $-A_1$, however, gives quantitatively the affinity of the reaction—

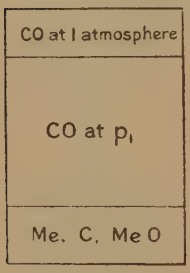


FIG. 51.

$$MeO + C \rightarrow Me + CO.$$

If we call A_2 the affinity per mole of oxygen of the second reaction as written, then $-A_2$ is what we want to measure, corresponding to the reaction—

$$2Me + O_2 \rightarrow 2MeO.$$

(The affinity reckoned per $\frac{1}{2}$ mole of oxygen is $\frac{1}{2}A_2$.) Further, putting A_3 as the affinity of reaction (3) per mole of oxygen, it follows that—

$$-A_1 = \tfrac{1}{2}A_2 + \tfrac{1}{2}A_3.$$

[If this equality of work terms did not hold good, then we could imagine a cyclic isothermal process, which would yield a continuous quantity of work, but this in contradiction to the Second Law.] The quantity which we wish to measure, namely, $-A_2$ is given by—

$$-A_2 = +2A_1 + A_3.$$

First of all we have to measure $\frac{1}{2}A_3$, *i.e.* the affinity of the reaction—

$$\tfrac{1}{2}O_2 + C \rightarrow CO.$$

[A_3 would be the affinity per *mole* of oxygen O_2.]

The dissociation of carbon monoxide, however, even at extremely high temperatures is immeasurably small; and we have thus to measure A_3 indirectly—by combining two other reactions whose individual affinities can be calculated. Let us take the reactions—

$$CO_2 = CO + \tfrac{1}{2}O_2 \quad . \quad . \quad . \quad . \quad (4)$$

and

$$2CO = C + CO_2 \quad . \quad . \quad . \quad . \quad (5)$$

by adding (4) and (5) we get—

$$CO = C + \tfrac{1}{2}O_2,$$

which is equation (3) reversed. Hence denoting by A_4 the affinity of reaction (4) per mole of oxygen (O_2), and A_5 the affinity of reaction (5) as it stands, we get—

$$-\tfrac{1}{2}A_3 = \tfrac{1}{2}A_4 + A_5.$$

Nernst and Wartenberg (*Zeitsch. physik. Chem.*, **56**, 548, 1906) have determined the dissociation of carbon dioxide into carbon monoxide and oxygen at temperatures from 1300° to 1500° absolute, and from the data have calculated the equilibrium for all other temperatures. The equilibria relations of equation (5) have been determined by Boudouard (*Comptes Rendus*, **128**, 842, 1899), so that the affinity A_3 is known. Now we know A_1 also, and hence $-A_2$ can be calculated.

Example.—What is the Affinity of Oxygen for Iron at Atmospheric Pressure and at a Temperature of 1000° abs.?

According to Schenk, Semiller and Falcke (*Ber.*, **40**, 1708, 1906), the equilibrium pressure of carbon monoxide for the reaction—

$$FeO + C \rightarrow Fe + CO$$

is—

T.	p_{1CO}.	$\log p_1$.
556° C.	73·2 mm.	1·866
596° C.	164·2 ,,	2·215
666° C.	386·0 ,,	2·566

From these numbers one obtains by exterpolation that at 1000° absolute, the equilibrium pressure of carbon monoxide is 810 mm. = 1·06 atmospheres. Evidently by replacing the carbon monoxide present by carbon monoxide at 1 atmosphere over the solids more carbon monoxide will tend to be formed, *i.e.* reduction of oxide takes place.

The affinity of the reaction, *i.e.* the work obtained by transferring 1 mole of carbon monoxide from a pressure of 1 atmosphere to a pressure of 1·06 atmospheres is

$$A_1 = RT \log \frac{1}{p_1} = - RT \log p_1$$
$$= - 1{\cdot}98 \times 2{\cdot}3 \times 1000 \times 0{\cdot}025 = - 114 \text{ calories.}$$
$$\therefore + 2A_1 = - 228 \text{ calories.}$$

The dissociation equilibrium of carbon dioxide may be obtained from Nernst's data (*Lehrbuch*, 5 Aufl., p. 680). At 1000° absolute carbon dioxide at atmospheric pressure is dissociated to the extent of $1{\cdot}58 \times 10^{-5}$ per cent., that is 1 mole of carbon dioxide yields a fraction $1{\cdot}58 \times 10^{-7}$ mole of carbon monoxide and $1{\cdot}58 \times 10^{-7}$ gram-atoms of oxygen, or $\frac{1{\cdot}58}{2} \times 10^{-7}$ mole of O_2. Hence the affinity with which 1 mole of carbon dioxide at atmospheric pressure would break up into 1 mole of carbon monoxide and $\frac{1}{2}$ mole of oxygen, also at atmospheric pressure, is at 1000°—

$$\tfrac{1}{2}A_4 = RT \log K - \Sigma\nu \log C.$$

$\Sigma\nu \log C$ vanishes because all the concentrations are unity as has been arbitrarily chosen, *i.e.* we have made use of the term 1 atmosphere. K must of course be calculated in pressure terms. Hence—

$$\tfrac{1}{2}A_4 = RT \log K = RT \log \frac{p_{CO} \times p_{O_2}^{\frac{1}{2}}}{p_{CO_2}}$$
$$= 2{\cdot}3 \times 1{\cdot}98 \times 1000 \times \log \left(\frac{1{\cdot}58 \times 10^{-7} \times \sqrt{\frac{1{\cdot}58}{2} \times 10^{-7}}}{1} \right)$$
$$= 2{\cdot}3 \times 1{\cdot}98 \times 1000 \times (- 10{\cdot}35)$$
$$= - 47{,}200 \text{ calories.}$$

The equilibrium pressure of the reaction—

$$2CO \rightarrow C + CO_2$$

is, according to Boudouard, 1 atmosphere at 1000° abs., the composition of the gas mixture being 67 volume per cent. of carbon monoxide, and 33 per cent. of carbon dioxide. In other words, the pressure exerted by the carbon monoxide is 0·67 atmosphere and the pressure of the carbon dioxide 0·33 atmospheres, the pressure of the carbon being of course extremely small. The equilibrium constant of the reaction at this temperature is

$$K = \frac{p_C \times p_{eCO_2}}{p^2_{eCO}} = \frac{p_C \times 0{\cdot}33}{(0{\cdot}67)^2}.$$

The work required to bring the system consisting of carbon monoxide and carbon dioxide each at 1 atmosphere pressure and in the presence of carbon (this system not being in equilibrium) into equilibrium is—

$$A_5 = RT \log K - RT\Sigma\nu \log C$$

$$= RT \log \frac{p_C}{1{\cdot}36} - RT \log \frac{p_C \times 1}{1^2} = - RT \log 1{\cdot}36$$

$$= - 2{\cdot}3 \times 1{\cdot}98 \times 1000 \times 0{\cdot}134 = - 610 \text{ calories.}$$

[That is, there is a negative tendency for carbon monoxide at 1 atmosphere pressure in contact with carbon and also in the presence of carbon dioxide at 1 atmosphere to dissociate into carbon and carbon dioxide, in other words, the reverse change (*i.e.* formation of carbon monoxide) will take place.]

The affinity of carbon for oxygen (at 1 atmosphere pressure), *i.e.* equation (3) $C + \frac{1}{2}O_2 \rightarrow CO$, forming carbon monoxide at a partial pressure of 1 atmosphere, is $\frac{1}{2}A_3$ where

$$\tfrac{1}{2}A_3 = - \tfrac{1}{2}A_4 - A_5 = + 47{,}200 + 610 = 47{,}810 \text{ calories.}$$

Finally the quantity we are aiming at, the affinity of oxygen (at 1 atmosphere pressure) for iron at 1000° abs., is given by $(-A_2)$, where—

$$- A_2 = + 2A_1 + A_3$$

$$= - 228 + 95{,}620$$

$$= + 95{,}392, \text{ which in round numbers} = 95{,}400.$$

The positive sign means that under the conditions of the experiment (1000° abs. and 1 atmosphere oxygen pressure) there is positive affinity between oxygen and iron, *i.e.* iron oxide will be formed. Note also that under the same conditions the affinity of oxygen per mole for carbon, *i.e.* $+ A_3$, is + 95,620, almost identical (numerically) with the affinity of oxygen for iron, being just a little greater.

Finally it may be pointed out that while by the union of 2 moles, *i.e.* gram-atoms, of iron to 1 mole of oxygen at 1 atmosphere, the free energy change is an evolution of 95,400 calories, the heat of reaction as determined by Le Chatelier is 129,900 calories, that is to say, considerably higher.

Another method of obtaining the affinity of oxygen for iron may be employed. The idea is the same as before except that instead of carbon, one uses hydrogen as the *reducing agent*, that is provided the affinity of hydrogen for oxygen is greater than the affinity of oxygen for the metal. (For details see Sackur, *loc. cit.*, pp. 64 and 65.)

Electrical Method of Measuring Affinity.

Having considered a few cases of affinity in which the determination is carried out by means of vapour pressure or concentration measurements, it is necessary to discuss the electrical method, especially as this may be employed in cases to which other methods are quite inapplicable. As already pointed out, if we take the faraday (96,540 coulombs) as the unit of electrical quantity, *i.e.* the quantity of electricity associated with 1 gram equivalent of any ion, and if the valency of the ion of the chosen substance be n, the electrical energy connected with the transformation of 1 gram ion is $n \times E$ or nE, where E is the electromotive

force of the cell in which the reaction is proceeding. The reaction in the cell must of course be a reversible one, as already explained in the chapter on the thermodynamic criteria of equilibria. The most familiar instance is that of the *Daniell Cell*, in which the following reaction takes place—

$$Zn_{metal} + Cu^{++} \rightarrow Zn^{++} + Cu_{metal}.$$

The ions in this case are divalent ($n = 2$). If E = e.m.f. of the cell, then the affinity (A) of the process in terms of 1 gram ion (the same as 1 gram-mole in this case) of either copper or zinc is 2E. When the reaction reaches an equilibrium the e.m.f. falls to zero, that is the affinity is zero as one would expect. If a Daniell cell be set up with the zinc sulphate or copper sulphate solutions of the same strength $\left(\text{say}\frac{N}{10}\right)$, the e.m.f. is approximately 1·1 volts. The affinity A of the process is therefore 2·2 volt faradays. This can very easily be converted into other units. Thus 1 faraday = 96,540 coulombs, and hence A = 212,390 volt-coulombs or joules. Further, 4·2 joules = 1 calorie, and hence A = 50,570 calories (per gram-ion or per gram atom of (say) zinc. The reaction which we are actually considering is the affinity of metallic zinc for a certain solution of copper sulphate. We might also regard it as measuring the relative affinities of the metals for electricity, *i.e.* their relative tendency to pass into the ionic state. The reaction reaches an equilibrium which may be denoted in the usual way—

$$Zn_{metal} + Cu^{++} \rightleftarrows Zn^{++} + Cu_{metal}$$

and the equilibrium constant is given by—

$$\frac{C_{ezn++} \times C_{cu}}{C_{ecu++} \times C_{zn}},$$

but since the "concentration" of the solid metal itself is necessarily a constant, we can simply write—

$$K = \frac{C_{ezn+}}{C_{ecu++}}.$$

If we have copper sulphate and zinc sulphate solutions in the cell at arbitrarily chosen concentrations, such that C_{zn++} and C_{cu++} denote respectively the metallic ion concentrations, then the affinity of the process at temperature T must be given by the van 't Hoff isotherm, *viz.*—

$$\begin{aligned} A = 2E &= RT \log K - RT\Sigma\nu \log C \\ &= RT \log \frac{C_{ezn++}}{C_{ecu++}} - RT \log \frac{C_{zn++}}{C_{cu++}}. \end{aligned}$$

Now suppose we choose the zinc sulphate and copper sulphate solutions at approximately the same strength (say decinormal), this will mean that the "arbitrary" concentrations of the ions are approximately the same, and therefore the second term vanishes. The e.m.f. in such

a case at room temperature (T = 298) is found by measurement to be approximately 1·1 volt, so that—

$$A = 2 \times 1{\cdot}1 = RT \log \frac{C_{\epsilon zn++}}{C_{\epsilon cu++}} = RT \log K.$$

The electrical method of measuring A is thus a very convenient way of obtaining the equilibrium constant. Working out the above example, we see that—

$$\log K = \frac{2{\cdot}2}{RT}.$$

Since 2·2 is expressed in volt-faradays, it is necessary to have RT also in the same units. This is done by putting—

$$R = 0{\cdot}86 \times 10^{-4}.$$

Hence
$$\log_e K = \frac{2{\cdot}2}{0{\cdot}86 \times 10^{-4} \times 298} = 85,$$

or
$$K = 10^{37}.$$

This means that when the Zn^{++} and Cu^{++} have reached equilibrium, the concentration of Zn^{++} is 10^{37} times that of Cu^{++}. It is evident therefore that in the ordinary precipitation of metallic copper from solution by metallic zinc, the solution will have become, to all intents and purposes, pure zinc sulphate, the copper being quantitatively precipitated. The equilibrium point in this case is so far shifted over to one side that it would be utterly hopeless to attempt to determine K directly by analysis. This is a striking illustration of the usefulness of the electromotive force method.

It is of interest to look at the affinity of the process occurring in the Daniell cell from the standpoint of the solution pressures of the metals zinc and copper. Suppose that a cell having the zinc sulphate and copper sulphate solutions at the same ionic concentrations (say normal) yields a total e.m.f. of E volts. Experiment shows that the copper is the positive electrode, and therefore current flows *inside* the cell from zinc to copper, and outside from copper to zinc. Let us neglect the P.D. at the contact of the solutions. The total e.m.f. E is then due to the two single P.D.'s at the zinc and copper electrodes respectively, *viz.* $\pi_{zinc} + \pi_{copper}$. Suppose a small virtual change in the system to take place, involving the transfer of δF faradays through the cell at constant temperature and volume. This current is imagined to pass from the zinc to the copper through the cell. We have to consider all the work terms, electrical and osmotic. Since the charge transferred is positive the electrical work is $-\pi_{zinc}\delta F - \pi_{copper}\delta F$, since the potential at the zinc electrode rises as we pass to solution, and we reckon work terms positive when the force assists the motion, negative when the force opposes the motion (as is the case at the zinc electrode). The osmotic work done in the sense of Nernst's theory is first the work term—

$$\delta m \mathrm{RT} \log \frac{\mathrm{P}_{zn}}{p_{zn++}}$$

(where $p_{zn}{}^{++}$ is the osmotic pressure of the zinc ions, P_{zn} the solution pressure of the electrode, and δm is the mass in moles of zinc corresponding to a charge $\delta\mathrm{F}$, *i.e.* $\frac{\delta \mathrm{F}}{\delta m}$ = the valency = n), this being the maximum work done in transporting δm equivalents of the metal zinc from the zinc electrode to the solution. Now transport δm moles of copper from the copper solution to the copper electrode. The maximum work is again—

$$\delta m \mathrm{RT} \log \frac{p_{cu++}}{\mathrm{P}_{cu}}.$$

The total "osmotic work" is the algebraic sum of these quantities, namely—

$$\delta m \mathrm{RT} \log \frac{\mathrm{P}_{zn}}{p_{zn++}} + \delta m \mathrm{RT} \log \frac{p_{cu++}}{\mathrm{P}_{cu}}.$$

The total virtual work done we can equate to zero, is—

$$\delta m \mathrm{RT} \log \frac{\mathrm{P}_{zn}}{p_{zn++}} + \delta m \mathrm{RT} \log \frac{p_{cu++}}{\mathrm{P}_{cu}} - \pi_{zn}\delta \mathrm{F} - \pi_{cu}\delta \mathrm{F} = 0,$$

or

$$\mathrm{E} = \frac{\mathrm{RT}}{n\mathrm{F}} \log \frac{\mathrm{P}_{zn}}{p_{zn++}} + \frac{\mathrm{RT}}{n\mathrm{F}} \log \frac{p_{cu++}}{\mathrm{P}_{cu}}$$

or

$$\mathrm{E} = \frac{\mathrm{RT}}{n\mathrm{F}} \log \frac{\mathrm{P}_{zn}}{\mathrm{P}_{cu}} - \frac{\mathrm{RT}}{n\mathrm{F}} \log \frac{p_{zn++}}{p_{cu++}}.$$

But we have assumed that we are dealing with a case in which the concentrations, and therefore the osmotic pressures, of the zinc and copper ions are identical. The last term therefore vanishes, and we are left with—

$$\mathrm{E} = \frac{\mathrm{RT}}{n\mathrm{F}} \log \frac{\mathrm{P}_{zn}}{\mathrm{P}_{cu}} = \frac{\mathrm{RT}}{n\mathrm{F}} \log \frac{\mathrm{C}_{zn}}{\mathrm{C}_{cu}},$$

where the terms C_{zn} and C_{cu} bear to P_{zn} and P_{cu} the same relation as concentration of ions in solution bears to the respective osmotic pressures. But we have seen that the affinity $\mathrm{A} = 2\mathrm{EF}$, or $2\mathrm{E}$ if F be taken as *unit* of current (charge).

Hence

$$\mathrm{A} = \frac{2\mathrm{RT}}{n} \log \frac{\mathrm{C}_{zn}}{\mathrm{C}_{cu}},$$

and since n, the valency of the ions, is 2, this expression becomes—

$$\mathrm{A} = \mathrm{RT} \log \frac{\mathrm{C}_{zn}}{\mathrm{C}_{cu}} = \mathrm{RT} \log \frac{\mathrm{P}_{zn}}{\mathrm{P}_{cu}}.$$

Further, we have seen that when the ionic concentration of the metallic ions is the same, the van 't Hoff isotherm likewise reduces to the form—

$$A = RT \log K$$

where K is the equilibrium constant of the reaction, *i.e.*—

$$K = \frac{C_{ezn\,++}}{C_{ecu\,++}}.$$

Hence

$$K = \frac{P_{zn}}{P_{cu}}.$$

That is, the equilibrium constant of the reaction is identical with the ratio of the solution pressures of the metals. Since we have shown that K is of the order 10^{37}, this extremely large number likewise represents the number of times the solution pressure of zinc is greater than the solution pressure of copper.

The greater the solution pressure P of a metal, the more completely will it throw out of solution the ions of a metal having a lower solution pressure. The precipitation will tend to become less complete the nearer the solution pressure values are to one another. Since the values for P for various metals follow the order of "electrolytic potential series," it is clear that two metals in close proximity in this series can only give rise to the phenomenon of incomplete precipitation when the one with the higher value of P is added to a solution of the ions of the one with a somewhat smaller P value.

In the case of the Daniell cell we have really assumed that the affinity is measurable in terms of the electromotive force. The validity of the electrical method (by comparison with other results obtained by different methods) has been carefully tested by Knüpffer and Bredig (*Zeitsch. physik. Chem.*, **26**, 255) in the case of the reaction between thallium chloride and potassium sulphocyanide—

$$\underset{\text{Sparingly soluble.}}{TlCl} + KCNS = \underset{\text{Sparingly soluble.}}{TlCNS} + KCl$$

which reaches an equilibrium point determinable by analysis. The equilibrium exists not only at a definite temperature, as in the case of equilibria having transition points, but as the temperature changes, is displaced gradually in one direction or other with a corresponding alteration in the concentrations of the dissolved potassium chloride and potassium sulphocyanide.

The above change was employed for the construction of a galvanic cell (Knüpffer and Bredig, *loc. cit.*).

Thallium Amalgam	KCNS solution saturated with TlCNS	KCl solution saturated with TlCl	Thallium Amalgam

whose e.m.f. was measured. *Assuming that the e.m.f. was a correct measure of the affinity* (in this case, since we are dealing with monovalent ions, the e.m.f. should be identical numerically with the affinity), the equilibrium constants for the temperatures of 39·9° C., 20° C., 0·8° C., were separately calculated from the van 't Hoff isotherm—

$$E = A = RT \log K - RT\Sigma\nu \log C$$

and were found to be respectively—

0·88	1·26	1·79

while purely analytical methods gave—

0·85	1·24	1·74

This agreement is very strong evidence for the accuracy of the assumption which is made above, that the electromotive force is a measure of the affinity.

Further, since K is a function of the temperature, then on working with constant concentrations and altering the temperature, *i.e.* keeping the $\Sigma\nu \log C$ the same, it is possible to imagine the case in which the first term may equal the second, and if such a point was reached A would equal 0, and if the electromotive force was a true measure of the affinity it should also be zero at this temperature. Knüpffer found, experimentally, using the cell described above, that the electromotive force was zero at 42·3° C., while the temperature calculated from the isotherm, at which, by starting with given arbitrary concentrations, and altering the temperature until these concentrations coincided with the equilibrium concentrations, it was calculated to be 41·3° C. This is very strong proof of the validity of the principle involved.

Electrometric measurements may likewise be employed to calculate the affinity of complex ion formation (*e.g.* silver cyanide complex). For details *cf.* Sackur, *loc. cit.*, p. 85, *seq.*

Gas Cells.

The affinity of hydrogen ion ($H^{\cdot}$) for hydroxyl ion (OH'), and the determination of the ionisation constant of water from electromotive force measurements will first be considered.

Take the following cell—

Inside

$$\leftarrow$$

$$H_2 \,\Big|\, \begin{matrix}1 \text{ Normal} \\ HCl\end{matrix} \,\Big|\, \begin{matrix}1 \text{ Normal} \\ NaOH\end{matrix} \,\Big|\, H_2$$

A considerable P.D. exists at the contact of the acid and the alkali (Nernst, *Zeitsch. physik. Chem.*, **14**, 155, 1894). When this is corrected for, however, the e.m.f. of this cell is 0·81 volt at room temperature, the hydrogen electrode dipping in the acid being the positive pole, *i.e.* current flows as indicated from alkali to acid, inside the cell. The pressure of the hydrogen gas is supposed to be the same in both cases. The chemical reaction which is taking place, and whose affinity we are measuring is—

$$H^{\cdot} + OH' \rightarrow H_2O.$$

Thus, from the right-hand electrode a gram-ion of hydrogen goes into solution leaving the electrode negatively charged. In the presence of normal NaOH, *i.e.* approximately normal OH', the $H^{\cdot}$ ion cannot exist in the free state owing to the small dissociation constant of water,

and therefore a great quantity of OH' is used up to form H_2O. The current travelling, however, from right to left is carried by $Na^{\cdot}$ ions, and $H^{\cdot}$ with it, and Cl' and OH' diffusing against it. At the left-hand electrode $H^{\cdot}$ loses its charge and goes off as gas; the total result is that hydrogen gas is used up at the right-hand electrode, an equivalent amount going off as gas at the left-hand electrode, whilst in the cell itself a gradual neutralisation of the alkali by the acid goes on. This neutralisation is caused by the transport of electricity by $Na^{\cdot}$ ions in one direction, and Cl' ions in the opposite,[1] and is to be distinguished from the natural diffusion which would of course go on apart from the e.m.f. production. Finally the whole system becomes a solution of sodium chloride of the same strength throughout, and when this stage is reached the e.m.f. is zero, the two electrodes being identical and acting in opposite directions. Considering the condition of things, whilst the e.m.f. is still constant (at the value 0·81 volt) the neutralisation process is confined to the surface of contact, the affinity A can be written—

$$A = RT \log_e K_1 - RT \log_e \frac{C_{H_2O}}{C_{H^{\cdot}} \times C_{OH'}}.$$

Here $K_1 = \dfrac{C_{\epsilon H_2O}}{C_{\epsilon H^{\cdot}} \times C_{\epsilon OH'}}$. The ionisation constant of water, which is denoted by K_w, is the product of the equilibrium concentration of $H^{\cdot}$ and OH' in pure water. That is—

$$K_w = C_{\epsilon H^{\cdot}} \times C_{\epsilon OH'},$$

so that

$$K_1 = \frac{C_{\epsilon H_2O}}{K_w}.$$

In the case under discussion the $H^{\cdot}$ ion in the acid and the OH' in the alkali are both normal (*i.e.* unity), dissociation being assumed complete for the sake of simplicity, so that their logarithms in the second term vanish. Hence we can write—

$$A = RT \log_e \frac{C_{\epsilon H_2O}}{C_{\epsilon H^{\cdot}} \times C_{\epsilon OH'}} - RT \log_e C_{H_2O}.$$

Further, since in any dilute aqueous solution we can regard the concentration of the water to be practically constant, the term $C_{H_2O} = C_{\epsilon H_2O}$, so that—

$$A = - RT \log_e C_{\epsilon H^{\cdot}} \times C_{\epsilon OH'} = - RT \log_e K_w.$$

$$\therefore 0{\cdot}81 = - 0{\cdot}86 \times 10^{-4} \times 290 \times 2{\cdot}303 \log_{10} K_w$$

whence $K_w = 10^{-14}$.

This agrees very well with the ionisation constant of water obtained

[1] Taken in conjunction with the fact that the passage of current causes hydrogen ion to be discharged at the left, and hydroxyl ion to be neutralised at the right by hydrogen ion entering the solution from the hydrogen gas supply at the right-hand electrode.

by other means (conductivity, hydrolysis, catalysis). By taking into account the solution pressure of hydrogen at the hydrogen electrode, and treating the system simply as a concentration cell in respect of $H^{\cdot}$ ions, we are led to the same result. Thus denoting by P_{H_2} the solution pressure of hydrogen, we can write the e.m.f. E as—

$$E = \frac{RT}{nF} \log \frac{P_{H_2}}{p_{H^{\cdot}} \text{ in normal alkali}} + \frac{RT}{nF} \log \frac{p_{H^{\cdot}} \text{ in N acid}}{P_{H_2}}$$

$$= \frac{RT}{nF} \log \frac{p_{H^{\cdot}} \text{ in acid}}{p_{H^{\cdot}} \text{ in alkali}} = \frac{RT}{nF} \log \frac{C_{H^{\cdot}} \text{ in acid}}{C_{H^{\cdot}} \text{ in alkali}}.$$

But $C_{H^{\cdot}}$ in the acid is unity, hence—

$$E = - \frac{RT}{nF} \log C_{H^{\cdot}} \text{ in alkali.}$$

Now under all circumstances (*i.e.* in any dilute aqueous solution) it is considered that $C_{H^{\cdot}} \times C_{OH'} = K_w$ (the ionisation constant of water), so that—

$$E = - \frac{RT}{nF} \log \frac{K_w}{C_{OH'}} \text{ in alkali,}$$

and since $C_{OH'}$ in the normal alkali is also unity—

$$E = - \frac{RT}{nF} \log K_w.$$

But $A = nEF$. $\therefore A = - RT \log K_w$ as before.

The affinity of $H^{\cdot}$ at normal concentration for OH' also at normal concentration, in aqueous solution, amounts to $- RT \log K_w$ or + 0·81 volt-faraday, or 18,620 calories per gram-ion or per gram-mole of water formed. The heat of the same reaction, which, it has already been shown, is necessarily the heat of neutralisation of one equivalent of a strong acid with a strong alkali, is 14,000 calories approximately.

The same result would have been obtained if we had used an oxygen electrode in both solutions, only that here the direction of the current would have been reversed. A third method consists in combining an oxygen and hydrogen electrode, thus—

$$\xrightarrow{\qquad\qquad} \quad H_2 \mid \text{Normal HCl} \mid O_2$$

Any other electrolyte may be used, but is not so good in practice as acid. In this cell hydrogen dissolves in the ionic state as also does the oxygen as OH', thereby giving water. Both gases are therefore used up in the process. The results can be calculated as before (see Sackur, *loc. cit.*, pp. 92, 93). Perhaps the simplest method is to assume the correctness of the standard calomel electrode and measure the e.m.f. of the combination—

$$H_2 \left| \begin{matrix} \text{Normal} \\ \text{NaOH} \end{matrix} \right| \text{Calomel}$$

or better still by using Allmand's alkaline standard half element Hg | HgO, thus obtaining the single potential H_2 | NaOH, from which, knowing the solution pressure of hydrogen or its "electrolytic potential," the concentration of $H^{\cdot}$ ions in the alkali can be calculated and hence the dissociation constant of water.

The hydrogen-oxygen or Knall-gas cell, as it is often called, offers a very striking illustration of the inapplicability of the Berthelot principle of considering heat as the measure of affinity.

Thus in the case of the cell,

$$\xrightarrow{\qquad\qquad}$$

$$H_2 \mid \text{Normal NaOH} \mid O_2$$

as already pointed out, hydrogen dissolves in the ionic state in the alkali, thereby leaving the pole negative. Oxygen also dissolves, leaving the oxygen pole positive. If E is the total electromotive force of the cell—

$$E = \frac{RT}{n} \log \frac{P_{H_2}}{p_{H^{\cdot}}} + \frac{RT}{n_1} \log \frac{P_{O_2}}{p_{OH'}}$$

or

$$E = RT \log \frac{P_{H_2}^{n} \cdot P_{O_2}^{n_1}}{p_{H^{\cdot}}^{n} \cdot p_{OH'}^{n_1}}.$$

(Neglecting the liquid P.D.) $n = 2$ for $H_2 = 2H^{\cdot}$ and $n_1 = 4$ for $O_2 = 2O'' = 4OH'$.

Evidently, therefore, if the gases oxygen and hydrogen, instead of being fed into the cell at atmospheric pressure, are introduced at a lower pressure, the e.m.f. of the cell will also be lower. [The solution tensions P_{O_2} and P_{H_2} will vary with the pressure at which the gases are maintained, since their solubility in the platinum varies with pressure.] In fact, if the pressures of the gases be reduced almost to zero the e.m.f. will almost disappear. Under such circumstances water may evidently be decomposed by currents at minimum e.m.f., it being only necessary to apply one which exceeds that of the cell itself by a very small amount. It is clear from this that the electrical energy obtainable through the formation of water from oxygen and hydrogen or necessary for its decomposition (the two being equal and of opposite sign) may assume any magnitude from zero to a certain value dependent on the pressures of the gases or their concentrations in the platinum. The heats of formation of water at constant pressure, on the other hand, are the same no matter at what pressure we work, and this is the most direct evidence that a simple relation cannot exist between the heat of reaction and the electrical energy obtained. (Le Blanc, *Electrochemistry*, p. 255. Le Blanc further shows that this decomposition at minimum e.m.f. is *not* in contradiction to the Second Law.)

Affinity of Oxidation and Reduction Processes.

The electrical method of measuring the affinity of oxidations and reductions which can be set up in the form of a cell, is identical with

previous affinity measurements, consisting again in the determination of the e.m.f. If into an aqueous solution containing, say, ferro and ferri salts an electrode be introduced which must not be attacked by any of the components taking part in the reaction (say, a platinum electrode) but is simply employed as a carrier of current to and from the cell, and if further a hydrogen or a calomel electrode be employed as the other half-element, then we have a cell such as—

$$\mathrm{Pt} \;\Big|\; \begin{matrix}\mathrm{Fe^{+++}}\\ \mathrm{Fe^{++}}\end{matrix} \;\Big\|\; \mathrm{H^{\cdot}} \;\Big|\; \mathrm{H_2}$$

the e.m.f. of which is a measure of the oxidation or reduction process taking place. In the particular case mentioned, in which the hydrogen electrode is used as one half element, the total reaction occurring in the cell may be represented by—

$$\mathrm{H_2 + 2Fe^{+++} \rightarrow 2H^{+} + 2Fe^{++}}$$

i.e. a reduction of ferri to ferro,

or $$\mathrm{2H^{+} + 2Fe^{++} \rightarrow H_2 + 2Fe^{+++}}$$

i.e. an oxidation of ferro to ferri.

The reaction in the two parts of the cell may also be represented thus—

$$\left|\begin{matrix}\mathrm{2Fe^{+++} + 2\ominus}\\ \mathrm{= 2Fe^{++}\ formed}\end{matrix}\right| \;\Big\|\; \left|\begin{matrix}\mathrm{H_2 - 2\ominus}\\ \mathrm{= 2H^{\cdot}\ formed}\end{matrix}\right| \Big\} \begin{matrix}\text{Reduction current}\\ \text{right to left}\end{matrix}$$

(+ 2⊖ means that two electrons come from the platinum to the ferri-ferro solution, and − 2⊖ on the hydrogen side denotes that two electrons are given up to the hydrogen electrode, the two effects occurring simultaneously),

or $$\mathrm{2Fe^{+++} + H_2 = 2H^{\cdot} + 2Fe^{++}.}$$

Similarly the oxidation process, with current flowing from left to right, can be represented—

$$\left|\begin{matrix}\mathrm{2Fe^{++} - 2\ominus}\\ \mathrm{= 2Fe^{+++}}\end{matrix}\right| \;\Big\|\; \left|\begin{matrix}\mathrm{2H^{\cdot} + 2\ominus}\\ \mathrm{= H_2}\end{matrix}\right|$$

$$\mathrm{2Fe^{++} + 2H^{\cdot} = 2Fe^{+++} + H_2.}$$

The equilibrium constant of the above reduction reaction is—

$$\mathrm{K = \frac{[Fe_\epsilon^{++}]^2 \times [H_\epsilon^{\cdot}]^2}{[H_{\epsilon 2}] \times [Fe_\epsilon^{+++}]^2}}$$

square brackets denoting concentration terms and the suffix ϵ denoting equilibrium state. And the affinity A is—

$$\mathrm{A = RT \log K - RT \log \frac{[Fe^{++}]^2 \times [H^{\cdot}]^2}{[H_2] \times [Fe^{+++}]^2}.}$$

A is the affinity per mole of hydrogen H_2. The e.m.f. E is the affinity per gram equivalent, *i.e.* $\mathrm{E = \frac{A}{2}}$.

$$\therefore E = \frac{RT}{2} \log K - \frac{RT}{2} \log \frac{[Fe^{++}]^2 \times [H^{\cdot}]^2}{[H_2] \times [Fe^{+++}]^2}.$$

Writing $$\frac{RT}{2} \log K = E'_0,$$

and $$E'_0 + \frac{RT}{2} \log \frac{[H_2]}{[H^{\cdot 2}]} = E_0$$

we obtain $$E = E_0 - \frac{RT}{2} \log \frac{[Fe^{++}]^2}{[Fe^{+++}]^2},$$

or $$E = E_0 - RT \log \frac{[Fe^{++}]}{[Fe^{+++}]}.$$

E_0 is the value of E of the cell when the Fe^{++} and Fe^{+++} are at the same concentration in the solution. E_0 is called the normal potential of the process. E is called the reduction potential. Of course, if we had been considering the reverse process, *i.e.* an oxidation, we would have written—

$$K_1 = \frac{1}{K} = \frac{[Fe_e^{+++}]^2[H_{e2}]}{[Fe_e^{++}]^2[H_e^{\cdot}]^2}$$

and would finally have obtained—

$$E = E_0 - \frac{RT}{2} \log \frac{[Fe^{+++}]^2}{[Fe^{++}]^2},$$

or $$E = E_0 - RT \log \frac{[Fe^{+++}]}{[Fe^{++}]}.$$

Reversible reduction and oxidation processes are always thus connected. Suppose that the actual conditions in the cell itself are such that a reduction is going on, yielding an e.m.f. of E. Then if an external e.m.f. E be applied in the opposite direction, the reduction process will stop, and on making the externally applied e.m.f. just greater than the direct e.m.f., an oxidation will take place. The above formula brings out the dependence of the oxidising force upon the concentration of the various components which are taking part in the reaction.

R. Peters (*Zeitsch. physik. Chem.*, **26**, 193, 1895) was the first to systematically examine oxidation and reduction processes in such cells under definite conditions. He used as one half of the element the normal calomel electrode, the value of which in absolute measure was taken to be 0·56 volts, the mercury being positive with respect to the solution. The cell might thus be diagrammatically represented—

$$Pt \;\Big|\; \begin{matrix} Fe^{+++} \\ Fe^{++} \end{matrix} \;\Big\|\; \begin{matrix} Hg_2Cl_2 \\ Hg_2{}^{++} \end{matrix} \;\Big|\; Hg$$

Suppose that the process occurring is a reduction of some of the ferri to ferro ions. The direction of the inside current will then be from right to left; or what is the same thing, the direction of electron transfer will be from the mercury to the platinum *outside* the cell. The reaction in each half of the cell is thus—

$$\left| \begin{array}{c} 2Fe^{+++} + 2\ominus \\ = 2Fe^{++} \text{ (formed)} \end{array} \right| \left| \begin{array}{c} Hg_2 - 2\ominus \\ \underset{\text{Metal}}{} \\ = Hg_2{}^{++} \text{ formed} \end{array} \right|$$

These processes can be represented by the chemical equation—

$$2Fe^{+++} + \underset{\text{Metal}}{Hg_2} = Hg_2{}^{++} + 2Fe^{++}.$$

The equilibrium constant K′ is thus—

$$K' = \frac{C^2_{\epsilon Fe^{++}} \times C_{\epsilon Hg_2{}^{++}}}{C^2_{\epsilon Fe^{+++}} \times \underset{\text{Metal}}{C_{\epsilon Hg_2}}},$$

or since $C_{Hg_2{}^{++}}$, and likewise $C_{Hg_2 \text{metal}}$, are constant, we can write—

$$K = \frac{C^2_{\epsilon Fe^{++}}}{C^2_{\epsilon Fe^{+++}}}$$

and therefore—

$$A = RT \log K - RT \log \frac{C^2_{Fe^{++}}}{C^2_{Fe^{+++}}}.$$

Since A is reckoned per mole of mercury ionised, the e.m.f. $E = \frac{A}{2}$, or—

$$E = \frac{RT}{2} \log K - RT \log \frac{C_{Fe^{++}}}{C_{Fe^{+++}}}.$$

Setting $\frac{RT}{2} \log K = E_0$, we obtain—

$$E = E_0 - RT \log \frac{C_{Fe^{++}}}{C_{Fe^{+++}}}.$$

Peters obtained a large number of results with ferri and ferro mixtures, as well as with other *ic* and *ous* ions. The following are a few of his results. The mixtures were made from a stock solution of $\frac{N}{10}$ ferrous chloride + $\frac{N}{10}$ hydrochloric acid (the acid being added to prevent hydrolysis), and a similar solution of $\frac{N}{10}$ ferric chloride + $\frac{N}{10}$ hydrochloric acid. In the experimental results quoted the current flows inside the cell from calomel to the platinum, that is, electrons pass from the platinum to the ferro-ferri solution, and therefore reduction takes place.

The values of E_0 are calculated on the assumption that the concentration ratio of the ions Fe^{++} and Fe^{+++} is the same as the ratio of the ferri and ferro salt concentration, which of course can only be regarded as an approximation. The applicability of the theory is, however, demonstrated by the constancy of the value E_0. The numerical value of K will be seen to be very great. This means that when the equilibrium is reached in ferro-ferri ion solution the ratio of ferro to

Ratio of Fe^{++}, and Fe^{+++} in Per Cent.		E = obs. e.m.f. of Cell (Platinum the Positive Pole) in Volts.	P.D. of the Ferri | Ferro Electrode in Volts.	E_0 Calculated from E obs. by Applying the Work Equation.	$\sqrt{K}$ Calculated $= \frac{C_{eFe^{++}}}{C_{eFe^{+++}}}$.
Ferri.	Ferro.				
0·5	99·5	0·296	0·856	0·428	
1	99	0·312	0·872	0·427	
2	98	0·331	0·891	0·428	Mean value $10^{7·45}$
10	90	0·375	0·935	0·430	
50	50	0·427	0·987	0·427	
90	10	0·483	1·043	0·428	
99	1	0·534	1·094	0·419 ?	

ferri must be very great, *viz.* over 10 million. It will thus be evident that in Peters' mixtures (even in that containing only 0·5% Fe^{+++}) there is too great a concentration of Fe^{+++}, and there is the tendency for reduction to take place.

Variation of Affinity with Temperature.

The variation of A, that is to say of nE when the reaction occurs in a cell (and n represents the number of faradays associated with the unit of mass considered), is easily found by simply applying the Gibbs-Helmholtz equation—

$$A - U = T\left(\frac{dA}{dT}\right)_v$$

or

$$A + Q_v = T\left(\frac{dA}{dT}\right)_v$$

since + U = decrease in internal energy = heat evolved at constant volume = $- Q_v$ on the notation previously employed. On substituting nE for A we obtain—

$$nE - U = nT\left(\frac{dE}{dT}\right)_v$$

an expression deduced by Helmholtz giving the connection between the e.m.f. of a cell and the heat of the chemical reaction occurring in the cell, if the reaction were carried out in a calorimeter, and the heat actually measured. This expression gives us the true relation of heat evolution to affinity. In a particular case, if the e.m.f. has a negligibly small temperature coefficient $\frac{dE}{dT} = 0$, approx., *e.g.* the Daniell cell, the e.m.f. becomes numerically equal to the heat, *i.e.* under this condition affinity and heat evolution are identical—Thomsen's Rule and Berthelot's Law.

Experimental Verification of the Helmholtz Relationship.

(Table taken from Sackur's *Chemische Affinität*, p. 78.)

Cell.	E Observed at 0° C. in Volts.	nE in Calories.	U Observed.	$\frac{dE}{dT}$ Observed Volt | 1° C.	$nT\frac{dE}{dT}$.	$nE - U$.
$Cu \mid CuSO_4 100H_2O \vdots 100H_2O ZnSO_4 \mid Zn$.	1·0962	50,530	50,110	$+ 0{\cdot}34 \times 10^{-4}$	+ 430	+ 420
$Cu \mid Cu(C_2H_3O_2)_2 Aq \vdots 100H_2O Pb(C_2H_3O_2) \mid Pb$	0·4704	21,960	16,520	$+ 3{\cdot}85 \times 10^{-4}$	+ 4,840	+ 5,440
$Ag \mid AgCl \vdots 50H_2O\ ZnCl_2 \mid Zn$ . . .	1·0171	46,900	49,080	$- 2{\cdot}1 \times 10^{-4}$	- 2,640	- 2,180
$Ag \mid AgBr \vdots 25H_2O\ ZnBr_2 \mid Zn$ . . .	0·84095	38,770	39,940	$- 10{\cdot}6 \times 10^{-4}$	- 1,330	- 1,170
$Hg \mid Hg_2Cl_2 KCl \vdots KOH, Hg_2O \mid Hg$ . .	0·1483	7,570	- 3,280	$+ 8{\cdot}37 \times 10^{-4}$	+ 11,280	+ 10,850

The last two columns should theoretically be identical, their agreement is verification of the Helmholtz relationship. The last-mentioned cell is particularly interesting in that the heat of the reaction is negative, although the same reaction can give rise to a positive electrical energy output. In this case the Berthelot Law absolutely breaks down.

CHAPTER XIII.

Systems not in equilibrium (*continued*)—Relation between the affinity and the heat of a reaction—Nernst's heat theorem and some of its applications.

The Relation of Total Energy to Free Energy.

The Thermodynamical Theorm of Nernst. (*Cf.* Nernst's "Applications of Thermodynamics to Chemistry," Silliman Lectures, 1906; also for a compendium of more recent results see the article by F. Pollitzer, *Ahrens Sammlung*, vol. 17, 1912.)

The fundamental problem of greatest interest in the domain of chemical energetics is that of the quantitative relation of the total or internal energy (decrease) U involved in a reaction to the free energy A, involved in the same reaction. Since the total energy change is identical with $\pm Q_v$, the heat absorbed or evolved in the reaction at constant volume,[1] the problem may be put in the slightly different way: What is the quantitative connection between the free energy change and the heat change in any given reaction, that is, *is it possible to calculate the free energy change from a measurement of the heat change?* We have already briefly considered this question in the foregoing chapter. The earliest and simplest view held by Joule and Thomson was that the two terms were identical, namely, that $A = -Q_v$. They found this conclusion fairly accurately borne out in the case of the reaction $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$ which takes place in the Daniell cell, but this agreement must be looked upon as accidental, due to the fact that the electromotive force of this cell happens to have practically no temperature coefficient. The simple equality breaks down completely in many other cases, *cf.* the foregoing table. We have already discussed briefly this Berthelot principle in connection with affinity. In many cases, especially in reactions between solids and liquids (*i.e.* the so-called condensed systems), the Berthelot principle holds fairly well, but breaks down completely in reactions occurring in gases or dilute solutions. To show the approximation to equality between the

[1] Reactions in general do involve a volume change. Suppose in the reaction in question the volume increases; we measure this volume increase and multiply by the pressure under which the expansion took place, thereby obtaining a work term which can be expressed in calories, say. This work W must have been done at the expense of the internal energy of the system, and hence if the observed heat (per gram equivalent) is Q, the value which it would have had if no volume change had taken place, namely, Q_v, is given by the equation $Q_v = Q + W$.

two terms A and Q_v, one may cite the following instances of reactions which take place in condensed systems capable of being set up in the form of cells and therefore permitting the direct measurement of A independently of the direct measurement of Q_v:—

Reaction.	A Volt-faradays.[1]	Q_v Volt-faradays.
$2Hg + PbCl_2 \rightarrow Pb + Hg_2Cl_2$	0·54	0·44
$2Ag + PbCl_2 \rightarrow Pb + 2AgCl$	0·49	0·52
$2Ag + I_2 \rightarrow 2AgI$	0·68	0·60
$Pb + I_2 \rightarrow PbI_2$	0·89	0·87

These values hold good for ordinary temperatures, but even in the case of condensed systems the approximate equality vanishes if we work at higher temperatures. Perhaps the most striking exception to the principle of the equality of A and Q_v or U is that furnished by the process of fusion or transition from one phase to another. At the melting point A is practically zero (the specific volume of the solid and liquid being generally pretty close to one another), whilst Q_v is usually a large number. The only accurate relation between A and Q_v or U is that furnished by the Gibbs-Helmholtz equation based on the First and Second Laws of Thermodynamics. This, as we have just seen, is—

$$A - U = T\left(\frac{dA}{dT}\right)_v.$$

When the free energy of the reaction is independent of temperature (as is nearly the case in the Daniell cell) the terms A and U become equal to one another. They must likewise be equal to one another at the absolute zero of temperature (T = o) even when the free energy does possess a temperature coefficient. These conditions show the restrictions necessary to be applied to the principle of Berthelot. The principle is absolutely true for all reactions at the absolute zero. This, however, as one can see, is of little practical value or importance. The fact that the principle holds even approximately at ordinary temperatures is due to the fact that our ordinary temperature is not so far removed from the zero. Although this principle as an accurate physical law can no longer be relied upon, nevertheless it would be in the highest sense unscientific to discard it altogether. It is to Nernst that we owe the most successful solution of the problem of finding out what is the correct law underlying the approximately true principle of

[1] A being an energy or work term should be represented in electrical terms by the product of volts × quantity of current. In the above cases 1 faraday is supposed to have passed through the cell corresponding to 1 gram equivalent of the reacting metals. This is assumed in the numerical values quoted. Q_v is first obtained in calories and then converted into volt-faradays.

Berthelot. To appreciate Nernst's thermodynamic theorem, as it is called, let us return for a moment to the Gibbs-Helmholtz equation—

$$A - U = T\left(\frac{dA}{dT}\right)_v.$$

In cases such as reactions occurring in cells in which it is easy to measure A and $\frac{dA}{dT}$ directly,[1] this equation is sufficient to allow us to calculate U, but on the other hand the equation is *not* sufficient to allow us to carry out the reverse process, namely, that of calculating A from an observation of U. It is, therefore, not a complete answer to the problem which we have set before us. The limitations to the information obtainable from this equation may be shown in a somewhat different way if we integrate the expression. After a slight transformation the equation can be written in the form—

$$T\frac{dA}{dT} - A = -U$$

or

$$\frac{T\frac{dA}{dT} - A}{T^2} = \frac{-U}{T^2}$$

which is the same as writing—

$$\frac{d}{dT}\left(\frac{A}{T}\right) = \frac{-U}{T^2}.$$

On integrating this between the temperature limits o and T, we obtain—

$$\frac{A}{T} = a - \int_0^T \frac{U}{T^2} dT$$

where a is an undetermined integration constant. Now it has been shown by experience that the heat evolved or absorbed, that is ± U, in any reaction which takes place in a condensed system (solid or liquid (note the restriction)), varies with the temperature at which the reaction is made to take place, and this variation can be expressed by a series of terms involving T raised to different powers, that is for reactions between solids or liquids we can write—

$$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \delta T^4, \text{ etc.}$$

U_0 being the value of U at the absolute zero. Substituting this expression for U in the integral one obtains—

$$\frac{A}{T} = a + \frac{U_0}{T} - \alpha \log T - \beta T - \frac{\gamma}{2}T^2 - \frac{1}{3}\delta T^3 - , \text{ etc.}$$

or

$$A = U_0 + aT - \alpha T \log T - \beta T^2 - \frac{\gamma}{2}T^3 - \frac{\delta}{3}T^4 - , \text{ etc.} \quad . \quad (1)$$

This expression gives A in terms of U or Q_v, but there still remains

[1] In this differential, volume is supposed to be kept constant.

the undetermined integration constant a to be reckoned with. It may be noted that the numerical values for the coefficients α, β, γ, etc., are most easily obtained from measurements of the specific heats of the solid or liquid reactants and resultants in any given reaction which occurs in a condensed system by making use of the Kirchhoff Law, namely—

$$\frac{dU}{dT} = C_1 - C_2$$

where C_1 is the heat capacity of the system before transformation, C_2 that after the transformation.

Since $U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \ldots$

$$\frac{dU}{dT} = \alpha + 2\beta T + 3\gamma T^2 + \text{etc.} = C_1 - C_2.$$

The integrated form of the Gibbs-Helmholtz equation, even when restricted to reactions in condensed systems (which restriction allows of the expression of U in terms which can be experimentally determined) is still not sufficient to solve completely the question of the quantitative relation between A and U; there remains the integration constant *a*. *The real significance of Nernst's Theorem lies in this, that it permits us to evaluate the integration constant a.*

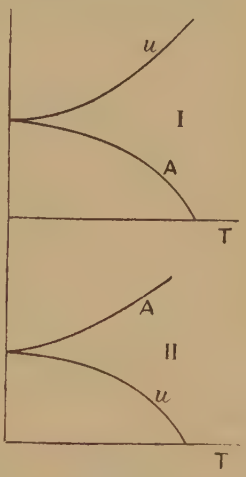


FIG. 52.

The theorem of Nernst may be stated in the following way: Not only are A and U identical at the absolute zero of temperature itself (as the Gibbs-Helmholtz equation requires), *but this equality also holds true for a short region above and in the neighbourhood of zero*, the curves for $\frac{dA}{dT}$ and $\frac{dU}{dT}$ coinciding for a short region and not simply touching one another at the absolute zero point only. This means that for a short range in the neighbourhood of zero, A and U remain constant and identical. This theorem of Nernst may be expressed graphically as in the figure [Fig. 52], in which the change of A and U with T is represented.[1] In the upper part of the diagram is represented the case in which A falls with rising temperature while U rises; in the lower part an instance of the reverse behaviour (which is also found in practice) is represented. Stated, analytically, Nernst's Theorem is—

$$\left.\begin{aligned} &\text{Limit } \frac{dA}{dT} = 0 \\ \text{and} \quad &\text{Limit } \frac{dU}{dT} = 0 \end{aligned}\right\} \text{ for } T = 0.$$

To see that if the A curve rises as the temperature increases the U

[1] In the figure it is to be supposed that the U and A lines run together and are horizontal for some distance above the zero value of T.

curve must fall, and *vice versa*, we proceed as follows. Writing down the Gibbs-Helmholtz equation—

$$A - U = T \cdot (dA/dT)$$

and differentiating with respect to temperature, we obtain—

$$dA/dT - dU/dT = dA/dT + T d^2A/dT^2$$

or

$$dU/dT = - T \cdot d^2A/dT^2.$$

These two terms are opposite in sign. Nernst assumes that the term A converges to a limiting finite value as the temperature falls to zero. It follows therefore that the sign of dA/dT and d^2A/dT^2 must be the same. Hence dU/dT is opposite in sign to dA/dT; or if A increases U will diminish, and *vice versa*.

The assumption that in the region of zero $dA/dT = dU/dT = 0$, has been shown by Nernst to be the necessary and sufficient condition for enabling us to calculate the integration constant a.

Thus, if we differentiate equation (1) with respect to T we obtain—

$$\frac{dA}{dT} = a - a - a \log T - 2\beta T - \tfrac{3}{2}\gamma T^2 - \tfrac{4}{3}\delta T^3 \quad . \quad (2)$$

and differentiating the expression—

$$U = U_0 + aT + \beta T^2 + \gamma T^3 + \delta T^4 \quad (2A)$$

one obtains—

$$\frac{dU}{dT} = a + 2\beta T + 3\gamma T^2 + 4\delta T^3 \quad . \quad . \quad .$$

Now introducing the Nernst Theorem—

$$\text{limit } \frac{dU}{dT} = \frac{dA}{dT} = 0 \text{ for } T = 0,$$

and in the neighbourhood of zero, it follows that—

$$a - a - a \log T - 2\beta T - \tfrac{3}{2}\gamma T^2 - \tfrac{4}{3}\delta T^3 = 0$$

and

$$a + 2\beta T + 3\gamma T^2 + 4\delta T^3 = 0.$$

In order that the two expressions may simultaneously be equal to zero, it is necessary that—

the integration constant $a = 0$

and also that $a = 0$.

Hence, allowing for this in equations (1) and (2A) one obtains finally—

$$U = U_0 + \beta T^2 + \gamma T^3 + \delta T^4 +, \text{ etc.} \quad . \quad . \quad (3)$$

$$A = U_0 - \beta T^2 - \frac{\gamma}{2} T^3 - \frac{\delta}{3} T^4 \quad . \quad . \quad . \quad . \quad (4)$$

Equations (3) and (4) are the solution to the problem regarding the calculation of A from determinations of U, that is from heat measurements alone, *i.e.* Q_v and specific heats.

The coefficients β and γ may be either positive or negative, and hence we have the two possibilities respecting the direction of the slope (up or down) of the curves for A and U shown in the diagram, where A and U are written as functions of temperature T.

As a result of calculation of A by the help of the above equations

(3) and (4) from observed values of U, it has been found that in a great many cases the coefficients β, γ, and δ are small. Hence, if the heat evolution in a given reaction is great, *i.e.* if U is great, both A and U tend to have almost the same value (U_0 approx.). It is this fact which lies at the basis of Berthelot's principle.

For the present we have of course to restrict the applications of equations (3) and (4) to the case of solid or liquid systems, for at the absolute zero, or in its neighbourhood, gases have no possible existence. This restriction is, however, not of such importance as it seems, for it is possible by the aid of the first two laws of thermodynamics to calculate the affinity of a reaction occurring in a gaseous system (or in a dilute solution) if we know the affinity and heat relations for the same reaction when it occurs in the solid state.

It must be remembered that the Nernst hypothesis is one which we cannot verify by direct experiment, for the simple reason that the measurement of A and U in the neighbourhood of the absolute zero cannot be carried out. We can, however, reach very low temperatures experimentally, and Nernst considers an extrapolation of such as justifiable.

Perhaps the most direct evidence which shows the rapid fall of specific heat with fall in temperature is offered by the two systems, benzophenone and betol. Both these substances show in a marked degree the phenomenon of super-cooling, so that it is possible to measure the specific heats of the solid and of the liquid forms at temperatures considerably below the true melting point. The total energy change (decrease) in passing from, say, the liquid to the solid state at any temperature, is represented by the symbol U, such a process being entirely analogous to any chemical reaction in which a substance A passes into another B. We have seen from the Kirchhoff Law that—

$$\frac{dU}{dT} = C_1 - C_2.$$

According to Nernst's Theorem $\frac{dU}{dT}$, and therefore the difference of the specific heats of the liquid and solid, tend to decrease towards zero as the temperature falls. This is borne out by the following experimental values of Koref:—

BENZOPHENONE.

T.	Specific Heat of Liquid.	Specific Heat of Solid.	$\frac{dU}{dt} = C_1 - C_2$.
295	0·3825	0·3051	0·0774
137	0·1526	0·1514	0·0012
BETOL (INTERPOLATED GRAPHICALLY).			
320	0·362	0·295	0·067
240	0·256	0·2205	0·0355
130	0·148	0·144	0·004

To illustrate the importance of Nernst's Theorem we shall consider a few well-known reactions, for which the heat effect U is known. From these data the values of A at various temperatures will be calculated and then compared with observed values of A, when such have been determined.

Applications of the Nernst Theorem to Condensed Systems.

1.—*The Transformation of Rhombic into Monoclinic Sulphur.*

Employing equation (3) in an abbreviated form, one finds for the total energy change involved in the transformation, say, of 1 gram of rhombic into monoclinic sulphur, the expression—

$$U = U_0 + \beta T^2$$

and therefore—

$$\frac{dU}{dT} = 2\beta T = C_1 - C_2$$

C_1 and C_2 being the specific heats of the two modifications. From measurements of these specific heats it is found that $\beta = 1{\cdot}15 \times 10^{-5}$. From Brönsted's[1] data for the heat of transformation at constant volume, *i.e.* Q_v or U, one obtains with a knowledge of β the value of U_0. The above equation for U takes, therefore, the form—

$$U = 1{\cdot}57 + 1{\cdot}15 \times 10^{-5}T^2.$$

(U with + sign denotes change from monoclinic to rhombic form.)

Nernst (*loc. cit.*), also Nernst's Text Book (English Translation of 6th German edition, p. 713 *seq.*), gives two instances of the application of this formula:—

T.	U Calculated.	U Observed.	Observer.
273	2·40	2·43	Brönsted
368	3·19	3·13	Tammann.

The agreement is good.

Further, by applying Nernst's second equation (equation 4), also in an abbreviated form, we have—

$$A = 1{\cdot}57 - 1{\cdot}15 \times 10^{-5}T^2.$$

At the transition temperature the free energy involved in a change from one modification to the other is zero, since the two forms are in equilibrium (except of course for the negligible amount of work done against the atmosphere, due to the slight volume change involved). By putting A = 0 we should be able to calculate the transition point by the aid of the above equation. Denoting this temperature by the symbol T_0 we have—

[1] *Zeitsch. physik. Chem.*, **56**, 645, 1906.

$$T_0 = \sqrt{\frac{1{\cdot}57}{1{\cdot}15 \times 10^{-5}}} = 369{\cdot}5 \text{ abs.}$$

T_0 observed $= 368{\cdot}4$ abs.

Nernst has further calculated by the aid of the expression for A the values corresponding to several temperatures for which A had been determined by Brönsted by means of solubility measurements. The following table contains the values thus obtained.

FREE ENERGY CHANGE IN CALORIES INVOLVED IN THE TRANSFORMATION OF SULPHUR FROM MONOCLINIC TO RHOMBIC FORM.

T Absolute.	A Calculated (Nernst).	A Observed (Brönsted).
273	0·72	0·71
288·5	0·64	0·61
291·6	0·63	0·59
298·3	0·57	0·55

Nernst has further shown that the observed values of $\frac{dU}{dT}$, *viz.* $(C_1 - C_2)$ over a wide temperature range down to 83° absolute is fairly accurately produced by the expression $2\beta T$. This is shown in the following table:—

T Absolute.	$\frac{dU}{dT}$ Observed.	$2\beta T = 2{\cdot}30 \times 10^{-5} T$.	Observer.
83	0·0854 − 0·0843 = 0·0011	0·0019	Nernst
93	0·0925 − 0·0915 = 0·0010	0·0021	"
138	0·1185 − 0·1131 = 0·0054	0·0032	Koref
198	0·1529 − 0·1473 = 0·0056	0·0046	Nernst
235	0·1621 − 0·1537 = 0·0084	0·0054	Koref
290	0·1774 − 0·1720 = 0·0054	0·0067	Wigand[1]
293	0·1794 − 0·1705 = 0·0089	0·0067	Koref
299	0·1809 − 0·1727 = 0·0082	0·0069	Wigand
329	0·1844 − 0·1764 = 0·0080	0·0076	Regnault

The comparison of theoretical conclusion with experimental results in the case of the transformation of sulphur has substantiated Nernst's Theorem regarding the possibility of calculating A from purely thermal data in a very satisfactory way. It will be observed that as T increases A decreases, finally becoming zero at the transition point. U, on the other hand, increases as T increases. The behaviour of this system is thus represented by the curves U and A belonging to type I. in the figure (Fig. 52).

[1] Wigand: *Annalen der Physik*, [4], **22**, 79.

2.—Application of Nernst's Theorem to the Calculation of the Temperature of Fusion of Single Substances.

At the melting point the solid and liquid are in equilibrium, that is A = 0, and therefore equation (4) becomes—

$$U_0 - \beta T^2 - \frac{\gamma}{2} T^3 = 0.$$

From measurements of the specific heat of the solid and (supercooled) liquid forms, C_1 and C_2 at various temperatures are obtained; and from these one obtains values of β and γ by means of the expression $C_1 - C_2 = 2\beta T + 3\gamma T^2$. This final term, $3\gamma T^2$, is generally negligible. From these data U_0 can be calculated. Employing the equation—

$$U = U_0 + \beta T^2 + \gamma T^3$$

and substituting the value of the latent heat of fusion Q_v or U at the melting point T, the temperature (T) required can be calculated.

The Process of Fusion.—The free Energy and total Energy Changes Involved.

Some examples of the application of the Nernst Theorem in a slightly different form to that already followed have been investigated by J. T. Barker (*Zeitsch. physik. Chem.*, **71**, 235, 1910) in Nernst's laboratory. The following table contains the values of A and $-Q_v$ (the latent heat of solidification (heat evolved)) in the case of benzene:—

SOLIDIFICATION OF BENZENE.

Absolute Temperature.	Latent Heat of Solidification in Calories per Mole. U.	A.
0	940	940
5	940·31	939·69
10	941·23	938·77
20	944·9	935·1
50	970·75	909·25
100	1063	817
150	1217	663
200	1430	450
250	1710	170
278·4 { ordinary melting point.	1900 { observed Q_v 2326 calories	0

The relation of A to U is that of type I. (Fig. 52). Other substances, such as naphthalene, show a closer agreement between Q calculated and observed than does benzene. The paper referred to should be consulted.

In the process of *fusion*, heat is absorbed, that is, the internal energy increases. Hence the internal energy of the liquid form is greater than

that of the solid. But the internal energy is given by $\int C_v dT$ where C_v is the specific heat at constant volume. Hence the specific heat of the liquid form is greater than that of the solid. In general, therefore, the *substances which are formed with absorption of heat have the larger specific heats.* This was first pointed out by van 't Hoff in 1904, though he made an erroneous assumption regarding the course of the U and A curves. In the following table are given a few data which illustrate the statement in the case of solids and liquids :—

Substance.	Solid C_v.	Liquid C_v.
Benzene	0·35	0·43
Lead	0·034	0·036
Bromine	0·084	0·11
Potassium	0·17	0·25
Naphthalene	0·33	0·44
Sodium nitrate . . .	0·28	0·41
Water	0·5	1·0

3.—*The Affinity of Water for certain Salts in the Production of Hydrated Salts.*

In the section on the measurement of affinity we have seen that the affinity per mole of a salt for water is given by the expression—

$$A = RT \log \frac{\pi}{p}$$

where π denotes the vapour pressure of water at the temperature T, and p the equilibrium pressure, *i.e.* the true vapour pressure of the salt, that is, the dissociation pressure of the next higher hydrate. To obtain A by the aid of Nernst's Theorem from purely thermal data one might proceed as follows : First of all obtain the heat of hydration of the given salt. This has been done very comprehensively and accurately by J. Thomsen (*Thermochemistry*, translated by Miss K. A. Burke. Ramsay's Series), who measured directly by calorimetric means the heat of solution of a given hydrate, and then the heat of solution of the anhydrous salt, or the next lower hydrate formed. The difference between these two heat values gives the desired heat of hydration in the production of the given hydrate. If we neglect or allow for any work done (at the expense of the heat energy) due to a volume change, we can easily obtain Q_v or U for the given instance. Now, if we have also data relating to the specific heat of water, of the hydrated salt in question, and of the next lower hydrate or anhydrous form we should know $\frac{dU}{dT}$ at several temperatures, and hence we could calculate the coefficients β and γ. Knowing U itself at one temperature together with β and γ we could obtain the value of U_0. Now knowing U_0, β, and γ,

equation (4) should give us at once the value of A required. The barrier to this procedure lies, however, in the fact that the specific heat of water is abnormal in its behaviour with respect to temperature, and hence Nernst (*Sitzungsber d. Berlin Akad. d. Wiss.*, **52**, 1906) has dealt instead with the closely allied problem of the affinity of *ice* for the salt in question, since the specific heat of ice is normal in behaviour. Its molecular heat is accurately represented by the equation—

$$C = 3{\cdot}0 + 0{\cdot}0223T \quad . \quad . \quad . \quad . \quad (5)$$

which allows us to extrapolate to temperatures higher than 0° C., *i.e.* into temperature regions where we would naturally have employed the specific heat of water had this been "normal". The values of Q_v obtained by Thomsen refer to the heat of hydration by liquid water. We must convert this into heat of hydration by ice. To do this we have to subtract from Thomsen's value the value of the molecular latent heat of fusion of ice at the given temperature. At 0° C. this is given by $\lambda_0 = 1440$ calories. The temperature coefficient of λ can be approximately calculated from the difference of the molecular heats of water and ice at 0° C., namely, $\frac{d\lambda}{dT}$. This works out to 9·0 calories per degree. Hence at 18°—the temperature to which many of Thomsen's data refer—the value of the latent heat of fusion is—

$$\lambda_{18^\circ} = 1440 + (18 \times 9{\cdot}0) = 1600 \text{ calories per mole.}$$

Hence the value of U required—the total energy change in the process of adding 1 mole of ice to the given anhydrous salt or hydrate—is easily obtained from the expression—

$$U = (Q_{\text{Thomsen}} - 1600) \text{ calories per mole.}$$

Now we want to apply the theorem to calculate A. Schottky (*Zeitsch. physik. Chem.*, **64**, 415, 1908), who has investigated several cases of this kind, uses equations (3) and (4) in their simplest forms, *viz.*—

$$\left.\begin{aligned} U &= U_0 + \beta T^2 \\ A &= U_0 - \beta T^2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3A)\ (4A)$$

whence

$$\frac{dU}{dT} = C_1 - C_2 = 2\beta T.$$

The reaction in general may be written—

$$\text{anhydrous salt} + H_2O_{ice} \rightarrow \text{hydrated salt}$$

or

$$\text{hydrated salt} + H_2O_{ice} \rightarrow \text{higher hydrated salt}$$

i.e.

$$(AB m H_2O) + H_2O_{ice} \rightarrow (AB(m+1)H_2O).$$

The term $2\beta T$ is the difference of the heat capacities of the two sides of the above equations. Taking the second case—

$$2\beta T = (C_{AB m H_2O} + C_{ice}) - C_{AB(m+1)H_2O}.$$

Now the difference of the specific or molecular heat terms $C_{AB(m+1)H_2O}$ and C_{ABmH_2O} is the heat capacity of the water of crystallisation which has been produced from the ice. Denoting this by C′ we obtain—

$$2\beta T = C_{ice} - C',$$

If we are dealing with the case of hydration of the anhydrous salt by the addition of 1 mole of ice—

$$2\beta T = C_{\text{anhydrous salt}} + C_{\text{ice}} - C_{\text{salt } H_2O}$$

where again $C_{\text{salt } H_2O} - C_{\text{salt}} = C'$ the heat capacity of the water of crystallisation

so that $$2\beta T = C_{\text{ice}} - C'.$$

Taking as a particular case the reaction—

$$CuSO_4 + 1H_2O \text{ ice} \rightarrow CuSO_4H_2O$$

Schottky found at 9° C., from equation (5), that—

$$C_{\text{ice}} = 9{\cdot}29 \text{ calories per mole}$$
$$C' = 6{\cdot}99 \text{ (Schottky), } 6{\cdot}60 \text{ (Fittig)}$$

and hence, using Schottky's C′ value—

$$\beta = \frac{9{\cdot}29 - 6{\cdot}99}{2 \times (273 + 9)} = 0{\cdot}00408.$$

From Thomsen's data U at 18° C. is 4860 calories per mole, and hence from equation (3A) we find—

$$U_0 = 4520 \text{ calories per mole}$$

and finally from equation (4A) $A = 4520 - 0{\cdot}00408T^2$

and therefore—

$A_{18° C.} = 4180$ } calories per mole. Using Fittig's value
$A_{78° C.} = 4010$ } of C′, $A_{78° C.} = 3810$ calories.
Mean $A_{78° C.} = 3910$ calories per mole.

It will be seen that A at 18° C. is less than U at the same temperature. They were identical, of course, at the absolute zero, the relation of the two in this case being therefore represented by curves of Type I. (Fig. 52).

We have now to compare the value of A obtained above from purely thermal data, with what may be called the observed value of A, namely, that obtained from vapour pressure measurements. The dissociation pressure p of $CuSO_4 . H_2O$ has been determined at 78° C., and found to be 2·5 mm. of mercury. (It is owing to this choice of temperature that it was necessary to calculate A from the thermal data also at 78° C.) Now we have to obtain the vapour pressure π which ice would possess, if it could be obtained as such, at 78° C. This is obtained accurately from Scheel's interpolation formula[1] (*Verh. d. D. physik. Gesell.*, **8**, 391, 1905)—

$$\log \pi = 11{\cdot}4796 - 0{\cdot}4 \log T - \frac{2687{\cdot}4}{T}.$$

[1] The experimental verification of Scheel's formula must, of course, refer to temperatures below 0° C. The following three observations are sufficient:—

$t°$ C.	Mm. Hg. π Calculated by Scheel.	Mm. Hg. π Observed.
0	4·58	4·58
− 10	1·97	1·97
− 50	0·031	0·034

With the aid of this formula we find

$$\pi_{78^\circ\,C.} = 639 \text{ mm. Hg.}$$

Hence—

$$A \text{ observed} = RT \log \frac{\pi}{p} = 1{\cdot}985 \times (273 + 78) \log \frac{639}{2{\cdot}5},$$

or A observed = 3860 calories per mole.

Mean value of A from thermal data = 3910 calories per mole.

The agreement is very good.

The affinity of H_2O (in the form of ice and also in the liquid form) for a given salt varies, as one might expect, according to the degree of hydration already possessed by the salt. This has been previously pointed out in the section on "Affinity," where the relative values for A obtained by dissociation pressure measurements are given in the case of copper sulphate and its hydrates. The molecular heat of the water molecules also differs, from molecule to molecule, *i.e.* it is not simply an additive property. The following table illustrates this. The numerical values refer to the H_2O molecule which is added to the corresponding salt (producing, of course, a higher hydrate).

Substance.	Molecular Heat (Schottky) at 9° C.	Molecular Heat (Fittig).
$CuSO_4$	24·09 calories	25·07
$CuSO_4 1Aq$	31·08 ,,	31·67
$CuSO_4 3Aq$	48·88 ,,	47·92
$CuSO_4 5Aq$	67·15 ,,	65·55
$CuSO_4 7Aq$	88·3 ,,	89·97

In general it may be pointed out that where A and U are very nearly the same—as is the case with some of the salts above mentioned and is likewise the case with a number of reactions which can be set up in the form of voltaic cells, *e.g.* the Daniell cell or the Clark cell—the accurate application of the Nernst Theorem is difficult owing to the smallness of the coefficients β and γ, which renders the expression (equations (3) and (4)) particularly sensitive to small errors of observation. For the purpose of simply testing the theorem it is only fair therefore to examine those cases in which A and U differ widely, *e.g.*—

$$CuSO_4 + H_2O \rightarrow CuSO_4 . H_2O.$$

4.—*Voltaic Cells consisting of Liquid or Solid Substances. Calculation of the Electromotive Force from Thermal Measurements.*

In the present case we are confining ourselves to cells the constituents of which are either solid or liquid, since the Nernst Theorem is directly applicable to these. In the first instance we must *not* take up those cases in which *solutions* are present, since at absolute zero it seems probable that each phase will consist of a single substance only.

Later it will be pointed out how the theorem may be extended even to gas cells. Convenient types of cells for our present purpose are the following—

Cell.	Chemical Reaction.
$\underset{\text{Solid.}}{Pb} \mid \underset{\text{Solid.}}{PbCl_2} \mid \underset{\text{Solid.}}{AgCl} \mid \underset{\text{Solid.}}{Ag}$	$Pb + 2AgCl \rightarrow 2Ag + PbCl_2$
$\underset{\text{Solid.}}{Ag} \mid \underset{\text{Solid.}}{AgI} \mid \underset{\text{Solid.}}{I_2}$	$Ag + I_2 \rightarrow 2AgI$

The Clark cell at the cryohydric point—

$\underset{\text{Solid.}}{Zn} \mid \underset{\text{Solid.}}{ZnSO_4 . 7H_2O} \mid \underset{\text{Solid.}}{Hg_2SO_4} \mid \underset{\text{Liquid.}}{Hg}$	$Zn + Hg_2SO_4 + 7H_2O_{(ice)} \rightarrow ZnSO_4 . 7H_2O + 2Hg.$

Let us consider the case of the Clark cell. This cell at ordinary room temperature contains the zinc salt in aqueous solution. We have already seen that it is desirable to work with a cell, each phase present being a single "pure" substance. To realise this in the Clark cell we must work at the cryohydric temperature, namely − 9° C., at which ice separates out. The reaction is indicated above. The following heat data are available (at 17° C.):—

Transformation of Zn into $ZnSO_4$, heat evolved . .	230,090 cals.
Transformation of $ZnSO_4$ into $ZnSO_4 . 7H_2O$, heat evolved	22,690 ,,
Total heat evolved =	252,780 ,,

Transformation of 7 moles of ice into water of crystallisation = approximately to heat of fusion per mole × 7 (heat absorbed) = (7 × 1580) . . =	11,060 cals.
Transformation of Hg_2SO_4 into Hg_2, heat absorbed =	175,000 ,,
Total heat absorbed =	186,060 ,,

Therefore the nett heat evolved per mole of zinc (say) by the above reaction = 66,720 calories. This value holds for 290° absolute. This is the total energy change (neglecting the very small volume change) per mole of zinc transformed. If we denote by U the total energy per gram equivalent, then U = 33,360 calories at 290° absolute.

Now we have to calculate β since we are only applying the theorem in its simplest form, *viz.*—

$$\left.\begin{aligned} U &= U_0 + \beta T^2 \\ A &= U_0 - \beta T^2 \end{aligned}\right\}$$

$$\left.\begin{matrix}\text{heat capacity of} \\ \text{reactants}\end{matrix}\right\} - \left\{\begin{matrix}\text{heat capacity of} \\ \text{resultants}\end{matrix}\right\} = \frac{dU}{dT} = 2\beta T.$$

The following data on the molecular heats of the substances concerned are quoted by Nernst (*Textbook*, English Translation of the 6th German Edition, p. 747).

$Zn = 6{\cdot}0$ (10° C.), $Hg_2SO_4 = 31{\cdot}0$ (50°), $7H_2O = 63{\cdot}7$ (10°), $ZnSO_47H_2O = 89{\cdot}4$ (10°), $2Hg = 13{\cdot}2$.

From these figures we find, on reckoning per gram equivalent, instead of per gram-mole that $2\beta T = -0{\cdot}95$ for T = 283 absolute.

These values, Nernst points out, are in several instances not very accurate, and further they do not all obtain for the same temperature. They must suffice, however. The Nernst Theorem thus gives for the case of the Clark cell—

$$U = 33{,}505 - 0{\cdot}0017T^2$$
$$A = 33{,}505 + 0{\cdot}0017T^2.$$

Employing this formula to calculate the free energy per equivalent, or what is numerically the same thing the electromotive force of the cell in volts, one finds for the cryohydric temperature 266° absolute—

$$E = 1{\cdot}4592 \text{ volts (calculated)}$$

and by direct observation E = 1·4624 volts (observed). The agreement is exceedingly satisfactory. Note that in this reaction, A increases with temperature, U decreases (Type II. Fig. 52). For further illustrations, *cf.* Nernst (*Sitzungsber. Berlin. Akad.*, Jan., 1909; *Journal der Physique*, *l.c.*, 1910), and Pollitzer, *Ahrens. Sammlung*). The following table contains the values of the e.m.f. of certain cells consisting of "pure" solid or liquid components first calculated by the aid of the theorem and secondly observed directly.

Chemical Reaction.	T.	E Calculated.	E Observed.
$Pb + 2AgCl \rightarrow 2Ag + PbCl_2$	290	0·4890	0·4891
$2Hg + 2AgCl \rightarrow Hg_2Cl_2 + 2Ag$	288	0·0437	0·0439
$Pb + I_2 \rightarrow PbI_2$	291	0·863	0·863
$2Ag + I_2 \rightarrow 2AgI$	291	0·681	0·678

Further work on similar types of cells has been carried out, in which not only is use made of the Nernst Theorem but likewise of the Einstein theory of atomic heat of solids (as modified by Nernst and Lindemann). This will be taken up after we have discussed Planck's Quantum Theory of radiation and Einstein's application of it to the heat capacity of solids (Vol. III.).

Application of Nernst's Theorem to Equilibria in Homogeneous Gaseous Systems or Dilute Solutions.

Although as already pointed out in several instances the theorem directly applies only to solid or liquid systems, it will be shown that it can also be extended to the calculation of the equilibrium constant K in a gaseous system, provided we know beforehand the heat of the reaction at a single temperature, the molecular heats of the gaseous substances at a few temperatures, and the integration constants of the integrated form of the Clapeyron vapour pressure expression, which has been discussed in an earlier part of this book. Suppose the reaction under discussion is the general one—

$$\nu_1 a + \nu_2 b = \nu'_1 c + \nu'_2 d.$$

If this reaction were taking place in a completely condensed system,

all the substances being single "pure" solids or liquids (liquid solutions being ruled out since at low temperatures these would probably separate into their single components), we could represent the total energy change (*i.e.* decrease) by the usual expression—

$$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 +, \text{ etc.}$$

If the same reaction were made to take place in the homogeneous gaseous state, we can express the total energy change (for the same number of molecules as before) by the term U′, where

$$U' = U'_0 + \alpha' T + \beta' T^2 + \gamma' T^3.$$

U'_0 represents the heat evolved by the reaction in the neighbourhood of the absolute zero. At the actual zero the existence of a gaseous state is supposed to be impossible. Now we have already seen that the affinity of a reaction such as the above occurring in a condensed system (liquid or solid) is given by a particular form of the van 't Hoff isotherm, *viz.*—

$$A = RT \log K - RT\Sigma\nu \log C,$$

where K is the equilibrium constant, namely—

$$\left[\frac{\text{Product of concentration of resultants raised to required powers}}{\text{Product of concentration of reactants raised to required powers}}\right]$$

for the reaction in the dilute gaseous state at the same temperature T; and C denotes the concentration of saturated vapour of each constituent separately. The term $\Sigma\nu \log C$ has the significance—

$$\nu'_1 \log C_c + \nu'_2 \log C_d \ldots - \nu_1 \log C_a - \nu_2 \log C_b.$$

Further we have already seen (p. 74) that the integration of the Clapeyron vapour pressure formula leads to values of C, the concentration of saturated vapour, which can be expressed for a single substance by the relation—

$$\log C = \frac{-\lambda_0}{RT} + \frac{\alpha_0}{R} \log T + \frac{\beta_0}{R} T + \frac{\gamma_0}{2R} T^2 + \ldots + i \quad . \quad (6)$$

in which "i" is a characteristic constant for the substance. The terms λ_0, α_0, β_0, γ_0 can be calculated from the relation $(\lambda_m - RT)$ = the molecular internal latent heat of vaporisation—

$$= \lambda_0 + \alpha_0 T + \beta_0 T^2 + \gamma_0 T^3.$$

where λ_0 denotes the internal molecular heat near absolute zero. It follows from the definition of the term $\Sigma\nu \log C$ that we can write—

$$\begin{aligned}
\Sigma\nu \log C = {} & \frac{-\nu'_1\lambda_{0_c}}{RT} + \frac{\nu'_1\alpha_{0_c} \log T}{R} + \frac{\nu'_1\beta_{0_c} T}{R} +, \text{ etc.} + \nu'_1 i_c \\
& \frac{-\nu'_2\lambda_{0_d}}{RT} + \frac{\nu'_2\alpha_{0_d} \log T}{R} + \frac{\nu'_2\beta_{0_d} T}{R} +, \text{ etc.} + \nu'_2 i_d \\
& \frac{+\nu_1\lambda_{0_a}}{RT} - \frac{\nu_1\alpha_{0_a} \log T}{R} - \frac{\nu_1\beta_{0_a} T}{R} -, \text{ etc.} - \nu_1 i_a \\
& \frac{+\nu_2\lambda_{0_b}}{RT} - \frac{\nu_2\alpha_{0_b} \log T}{R} - \frac{\nu_2\beta_{0_b} T}{R} -, \text{ etc.} - \nu_2 i_b
\end{aligned}$$

or more briefly—

$$\Sigma\nu \log C = \frac{-\Sigma\nu\lambda_0}{RT} + \frac{\Sigma\nu a_0 \log T}{R} + \frac{\Sigma\nu\beta_0 T}{R} + \frac{\Sigma\nu\gamma_0 T^2}{2R} + \Sigma\nu i \quad (6A)$$

Employing the van 't Hoff isotherm in the form given above, we obtain—

$$RT \log K = RT\Sigma\nu \log C + A.$$

Now the affinity A of a reaction occurring in a condensed system is given by Nernst's Theorem—note at this point the theorem is introduced—viz.—

$$A = U_0 - \beta T^2 - \frac{\gamma}{2}T^3.$$

Hence we can write after substitution, using equation (6A)

$$RT \log K = -\Sigma\nu\lambda_0 + \Sigma\nu a_0 T \log T + \Sigma\nu\beta_0 T^2 + \frac{\Sigma\nu\gamma_0}{2}T^3 + RT\Sigma\nu i + U_0 - \beta T^2 - \frac{\gamma}{2}T^3.$$

That is,

$$RT \log K = (U_0 - \Sigma\nu\lambda_0) + \Sigma\nu a_0 T \log T - (\beta - \Sigma\nu\beta_0)T^2 - \left(\frac{\gamma}{2} - \frac{\Sigma\nu\gamma_0}{2}\right)T^3 + RT\Sigma\nu i \quad . \quad . \quad . \quad . \quad (7)$$

Equation (7) may be regarded as the expression for the equilibrium constant of a dilute gaseous reaction obtained by the application of the Nernst Theorem to the van 't Hoff isotherm for the same reaction, when carried out in the liquid or solid state.

Now we have already seen, in the earlier part of this book, in dealing with the problem of the effect of temperature on the equilibrium constant of a *gaseous* reacting system, that such is given by the reaction isochore, *viz.*—

$$\frac{-U'}{RT^2} = \frac{\partial \log K}{\partial T}.$$

This equation on integration (see below) contains an integration constant I, to the evaluation of which thermodynamical considerations (1st and 2nd Laws) have nothing to say. Hitherto the only way of obtaining I was by actually measuring K for at least one temperature. Now, however—and in this lies the great advance made by the application of the Nernst Theorem to the calculation of K—*we can show how the I of a reaction may be calculated beforehand quite apart from the reaction itself, if we only know the vapour-pressure-temperature relations of each of the substances separately.* This is effected as follows:—

We have seen in an earlier section (p. 116) that the integrated form of the isochore (quite independent of Nernst's Theorem, of course) for the gaseous reaction may be written—

$$RT \log K = U'_0 - \alpha' T \log T - \beta' T^2 - \frac{\gamma'}{2}T^3 -, \text{ etc. } + RTI \quad (8).$$

The significance of the coefficients is evident from the equation—

$$U' = U'_0 + \alpha'T + \beta'T^2 + \gamma'T^3,$$

U' being the heat evolved at constant volume or decrease in total energy, in the reaction in the homogeneous gaseous state. Now equations (7) and (8) are both expressions for the same quantity RT log K. They must be identical. Equating the coefficients of like terms, we find that—

$$\begin{aligned} U'_0 &= (U_0 - \Sigma\nu\lambda_0) \\ -\alpha' &= \Sigma\nu\alpha_0 \\ -\beta' &= -\beta + \Sigma\nu\beta_0 \\ -\gamma' &= -\gamma + \Sigma\nu\gamma_0 \end{aligned}$$

and $$I = \Sigma\nu i$$

The important relation for our present purpose is the last one. It shows that (on the basis of Nernst's Theorem) the sum of the integration constants of the *vapour pressure curves* which can be directly determined may be used to calculate the constant I for a given gaseous reaction, *without actually carrying the reaction out at all.* We can thus rewrite the integrated form of the reaction isochore (*viz.* equation (8)) in the form—

$$RT \log K = U'_0 - \alpha'T \log T - \beta'T^2 - \frac{\gamma'}{2}T^3 + RT\Sigma\nu i$$

or

$$\log K = \frac{U'_0}{RT} - \frac{\alpha'}{R}\log T - \frac{\beta'}{R}T - \frac{\gamma'}{2R}T^2 + \Sigma\nu i \qquad (9)$$

For practical convenience we can convert natural logarithms $\log_e$ into $\log_{10}$, and the expression becomes—

$$\log_{10} K = \frac{U'_0}{4{\cdot}571T} - \frac{\alpha'}{1{\cdot}985}\log_{10} T - \frac{\beta'}{4{\cdot}571}T - \frac{\gamma'}{9{\cdot}14}T^2 + \frac{\Sigma\nu i}{2{\cdot}3023} \qquad (9A)$$

K denotes a ratio of concentration terms, namely, $\dfrac{C_c^{\nu_1}C_d^{\nu_2}}{C_a^{\nu_1}C_b^{\nu_2}}$.

For greater convenience it is sometimes advisable to work in terms of partial pressures. The equilibrium constant is now K_p, where—

$$K_p = \frac{p_c^{\nu_1}p_d^{\nu_2}}{p_a^{\nu_1}p_b^{\nu_2}}.$$

Assuming the applicability of the gas law for each of the constituents, we can write $p = RTC$, and hence—

$$K_p = \frac{C_c^{\nu_1} \times C_d^{\nu_2} \times RT^{\nu_1+\nu_2+\ldots}}{C_a^{\nu_1} \times C_d^{\nu_2} \times RT^{\nu_1+\nu_2+\ldots}} = KRT^{\Sigma\nu}.$$

Hence $\log_{10} K_p = \log_{10} K + \Sigma\nu \log_{10} R + \Sigma\nu \log_{10} T$.

So that equation (9A) may be written—

$$\log_{10} K_p = \frac{U'_0}{4{\cdot}571T} - \frac{(\alpha' - \Sigma\nu R)}{R}\log_{10} T - \frac{\beta'T}{4{\cdot}571} - \frac{\gamma'}{9{\cdot}14}T^2 + \frac{\Sigma\nu(i + \log_e R)}{2{\cdot}3023}.$$

The expression $\frac{\Sigma\nu(i + \log_e R)}{2{\cdot}3023}$ is denoted by $\Sigma\nu C_0$, where C_0 is the chemical constant of any particular substance, values of which, as we have already seen, are given in an earlier part of this volume (p. 75). On making this slight substitution, we obtain finally for the integration of the isochore with the help of Nernst's Theorem—

$$\log_{10} K_p = \frac{U'_0}{4{\cdot}571T} - \frac{(\alpha' - \Sigma\nu R)}{R}\log_{10} T - \frac{\beta'}{4{\cdot}571}T - \frac{\gamma'}{9{\cdot}14}T^2 + \Sigma\nu C_0 \quad . \quad . \quad . \quad (9B)$$

Equations (9), (9A), (9B), and (9C) which follow, are of course all equivalent. A few words more with regard to the numerical evaluation of the coefficients which occur in the above.

We have seen that $\alpha' = -\Sigma\nu a_0$, where a_0 is obtained directly from the vapour pressure curve of each substance (equation (6)), from which C_0 is also obtained.[1] The expression—

$$\alpha' - \Sigma\nu R = -\Sigma\nu a_0 - \Sigma\nu R = -\Sigma\nu(a_0 + R)$$

Nernst puts $(a_0 + R) = 3{\cdot}5$ (calories) as an approximation (which is probably only a rough one, *cf.* Haber, *Thermodynamics of Technical Gas Reactions*, appendix to Lecture 3; also Nernst, *Applications of Thermodynamics to Chemistry*, p. 77). Hence—

$$(\alpha' - \Sigma\nu R) = -\Sigma\nu\, 3{\cdot}5$$

and

$$\frac{(\alpha' - \Sigma\nu R)}{R}\log_{10} T = -\Sigma\nu\, 1{\cdot}75 \log_{10} T$$

when R has been taken to be 2 calories. Equation (9B) can therefore be written—

$$\log_{10} K_p = \frac{U'_0}{4{\cdot}571} + \Sigma\nu\, 1{\cdot}75 \log_{10} T - \frac{\beta'}{4{\cdot}571}T - \frac{\gamma'}{9{\cdot}14}T^2 + \Sigma\nu C_0 \quad (9C)$$

Knowing the molecular heats of the gaseous reactants and resultants at a few temperatures, we can calculate α', β', and γ', since—

[1] That α' is really identical with $-\Sigma\nu a_0$ may be illustrated by taking an actual case, namely, the reaction $H_2 + I_2 \rightarrow 2HI$, all the substances being gaseous, and the reaction regarded as occurring at a very low temperature in the neighbourhood of absolute zero. α' stands for the molecular heat of the *gaseous* reactants *minus* the molecular heat of the *gaseous* resultants. That is—

$$\alpha' = C_{H_2}\text{ gas} + C_{I_2}\text{ gas} - 2C_{HI}\text{ gas},$$

The term $\Sigma\nu a_0$ is defined on p. 331 as equal to the expression—

$(C_{H_2}\text{ liquid} - C_{H_2}\text{ gas}) + (C_{I_2}\text{ solid} - C_{I_2}\text{ gas}) - (2C_{HI}\text{ liquid} - 2C_{HI}\text{ gas})$,

where the symbol C also denotes molecular heat.

But in the neighbourhood of absolute zero, the Nernst Heat Theorem states that the molecular heats of the *condensed* (liquid or solid) reactants *minus* the molecular heats of the *condensed* resultants is zero, for in the limit $\frac{dU}{dT} = 0$.

That is, $(C_{H_2}\text{ liquid} + C_{I_2}) - (2C_{HI}\text{ liquid}) = 0.$

Hence $\Sigma\nu a_0 = -C_{H_2}\text{ gas} - C_{I_2}\text{ gas} + 2C_{HI}\text{ gas}$

or $\Sigma\nu a_0 = -\alpha'.$

$$\left.\begin{array}{l}\text{Molecular heat capacity of}\\ \text{reactants} - \text{Molecular heat}\\ \text{capacity of resultants}\end{array}\right\} = \frac{dU'}{dT} = \alpha' + 2\beta'T + 3\gamma'T^2 + \ldots$$

Knowing these coefficients, and likewise knowing the total energy change (for the gaseous reaction) U′ at a given temperature T, we can calculate U'_0 by means of the familiar relation—

$$U' = U'_0 + \alpha'T + \beta'T^2 + \gamma'T^3 \ldots$$

As a matter of fact, the factor γ' may be neglected in general, and in some cases even β'. Referring again to equation (9c), it should be noted that for reactions (gaseous) in which there is no change in the number of molecules (*e.g.* $H_2 + Cl_2 = 2HCl$) the term $\Sigma\nu\ 1{\cdot}75\ \log_{10}T$ necessarily becomes zero. The terms $\Sigma\nu C_0$ as well as β' are not, however, necessarily zero for this or any other type of reaction.

It must be clearly borne in mind that the vital point of the problem under discussion lies in the possibility of calculating the isochore integration constant I from the characteristic $\Sigma\nu i$ or the chemical constants $\Sigma\nu C_0$ of the substances taking part. This, as already pointed out, is the conclusion arrived at by applying the Nernst Theorem to reactions in the gaseous state. Nernst, himself, has pointed out (*Applications of Thermodynamics to Chemistry*, p. 55) that Le Chatelier, even as early as 1888, had appreciated the significance of the constant I, and "seems also to have had some idea of the method of its solution". The following are Le Chatelier's words:—

"It is very probable that the constant of integration [I], like the coefficients of the differential equation [the Gibbs-Helmholtz equation] is a definite function of certain physical properties of the reacting substances. The determination of the nature of this function would lead to a complete knowledge of the laws of equilibrium; it would make it possible to determine, *à priori*, all the conditions of equilibrium relating to a given chemical reaction without the addition of new experimental data."

Examples of the Applicability of Nernst's Theorem to Homogeneous Chemical Equilibria.

1. *The Dissociation of Water Vapour.*

The reaction is $2H_2O \rightarrow 2H_2 + O_2$.

$$K_p = \frac{(p_{eH_2})^2(p_{eO_2})}{(p_{eH_2O})^2}$$

these partial pressure terms being equilibrium values. If x is the degree of dissociation under 1 atmosphere total pressure, then—

$$K_p = \frac{x^3}{2}$$

(since the degree of dissociation is very small). Experiment has shown that at 1300° absolute, and under 1 atmosphere pressure,

$$x = 0{\cdot}29 \times 10^{-4}.$$
$$\therefore K_p = 1{\cdot}218 \times 10^{-14}$$

and $$\log_{10} K_p = -13{\cdot}91.$$

We shall now proceed to calculate $\log_{10} K_p$ from equation (9c). Experimental data give us the following—

$U'_0 = -114{,}500$ calories per 2 moles of water vapour.

[N.B.—The negative sign denotes an increase in total energy or *absorption* of heat. This is what one would expect on the Le Chatelier principle for the dissociation of water, since the extent of the dissociation is known to *increase* as the temperature *rises*.]

Further
$$\beta' = -0{\cdot}00128$$
$$\gamma' = +6{\cdot}7 \times 10^{-7}$$
$$\Sigma\nu = (2 \text{ moles of } H_2 + 1 \text{ mole of } O_2 - 2 \text{ moles } H_2O) = 1.$$
$$\therefore \Sigma\nu\, 1{\cdot}75 \log_{10} T = 1{\cdot}75 \log_{10} T.$$

The chemical constant C_0 per mole of $H_2 = 2{\cdot}2$.
$$\therefore \text{ for 2 moles, } 2C_0 = 4{\cdot}4$$
$$C_0 \text{ per mole of } O_2 = 2{\cdot}8$$
$$C_0 \text{ per mole of } H_2O \text{ (gas)} = 3{\cdot}7.$$
$$\therefore \text{ for 2 moles, } 2C_0 = 7{\cdot}4.$$
$$\therefore \Sigma\nu C_0 = 4{\cdot}4 + 2{\cdot}8 - 7{\cdot}4 = -0{\cdot}2.$$

Equation (9c) becomes therefore—

$$\log_{10} K_p = \frac{-114{,}500}{4{\cdot}571T} + 1{\cdot}75 \log_{10} T + \frac{0{\cdot}00128T}{4{\cdot}571} - \frac{6{\cdot}7 \times 10^{-7}T^2}{9{\cdot}14} - 0{\cdot}2,$$

or
$$\log_{10} K_p = \frac{-25050}{T} + 1{\cdot}75 \log_{10} T + 0{\cdot}00028T - 0{\cdot}2$$

neglecting the γ' term.

For the temperature 1300° absolute this equation gives the value—

$$\log_{10} K_p = -14{\cdot}00$$

while
$$\log_{10} K_{p \text{ observed}} = -13{\cdot}91.$$

The agreement is very satisfactory. It should be pointed out that the last three terms on the right-hand side are often small compared with the first two. This is in a sense unfortunate, since it is just the final term which particularly interests us.

2. *The Deacon Process of Chlorine Manufacture.*[1]

The reaction is—

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

[1] *Cf.* Vogel v. Falkenstein, *Zeitsch. Elektrochemie*, 12 763, 1906.

This reaction may theoretically be split up into the two simpler reactions—

$$2H_2O = 2H_2 + O_2$$
$$2HCl = H_2 + Cl_2.$$

For the first reaction—

$$\log_{10} K_1 = \log_{10} \left(\frac{p^2_{H_2} \times p_{O_2}}{p^2_{H_2O}} \right)$$

(these partial pressures being, of course, equilibrium terms). It has just been shown that—

$$\log_{10} K_1 = \frac{-25050}{T} + 1{\cdot}75 \log T - 0{\cdot}00028T - 0{\cdot}2.$$

For the second reaction—

$$\log_{10} K_2 = \log_{10} \left(\frac{p_{H_2} \times p_{Cl_2}}{p^2_{HCl}} \right)$$

and it has been found that—

$$\log_{10} K_2 = \frac{-9626}{T} - 0{\cdot}8.$$

In this the β' as well as the γ' term is omitted as negligible. Also, since there is no change in the number of molecules, the expression $\Sigma\nu\ 1{\cdot}75 \log_{10} T = 0$ (though of course $\Sigma\nu C_0$ is not zero).

For the Deacon Process itself we have—

$$K_{p\ \text{Deacon}} = \frac{p^2_{H_2O} \times p^2_{Cl_2}}{p^4_{HCl} \times p_{O_2}}.$$

(these partial pressure terms being equilibrium values). This may be rewritten—

$$K_{p\ \text{Deacon}} = \frac{p^2_{H_2O} \times p^2_{Cl_2} \times p^2_{H_2}}{p^4_{HCl} \times p_{O_2} \times p^2_{H_2}}$$

that is— $$K_{p\ \text{Deacon}} = \frac{K_2^2}{K_1}$$

$$\therefore \log_{10} K_{p\ \text{Deacon}} = 2 \log_{10} K_2 - \log K_1.$$

Using the above data, one finds—

$$\log_{10} K_{p\ \text{Deacon}}$$
$$= 2\left(\frac{-9626}{T} - 0{\cdot}8\right) - \left(\frac{-25050}{T} + 1{\cdot}75 \log T + 0{\cdot}00028T - 0{\cdot}2\right),$$

$$\text{or } \log_{10} K_{p\ \text{Deacon}} = \frac{+5790}{T} - 1{\cdot}75 \log T - 0{\cdot}00028T - 1{\cdot}4.$$

The following table, given by Nernst (*Applications of Thermodynamics to Chemistry*, p. 89), shows the agreement between the values thus calculated and those experimentally determined in an exceedingly accurate manner by Vogel v. Falkenstein :—

$t°$ C.	K_p Deacon Observed.	K_p Deacon Calculated.	log K_p Deacon Observed.	log K_p Deacon Calculated.
450	31·0	31·9	1·49	1·50
600	0·893	0·98	− 0·050	− 0·009
650	0·398	0·371	− 0·400	− 0·430

3. *The Dissociation of Iodine Vapour.*[1]

The reaction is—

$$I_2 = 2I.$$

Exceedingly accurate measurements of the equilibrium constant at various temperatures ranging from 800° C. to 1200° C. were made, the following being the observed values of K_p in partial pressure terms :—

800° C.	900° C.	1000° C.	1100° C.	1200° C.
$K_p = 0·0114$	0·0474	0·165	0·492	1·23

Measurements of $K = \frac{C_I^2}{C_{I_2}}$ were also carried out, and from these by employing the isochore equation in its unintegrated form over small temperature ranges, in which U′ was considered to remain constant, *viz.*—

$$\frac{\partial \log K}{\partial T} = \frac{-U'}{RT^2}$$

values of U′ were obtained.

Equation (9c) is written by Bodenstein after substitution of numerical values thus—

$$\log_{10} K = \frac{-35480}{4·571T} + 1·75 \log_{10} T - \frac{0·0019}{4·571}T + \Sigma\nu C_0.$$

The term $\Sigma\nu C_0$ is, according to Bodenstein, + 0·422. Employing this equation one can calculate $\log_{10} K_p$.

The following table shows the very good agreement obtained between observed and calculated values :—

Absolute Temperature.	1073°.	1173°.	1273°.	1373°.	1473°.
$\log_{10} K_p$ observed . .	− 1·915	− 1·325	− 0·782	− 0·309	− 0·091
$\log_{10} K_p$ calculated . .	− 1·956	− 1·34	− 0·771	− 0·311	− 0·084

Note, on the calculation involved in the above.—For the actual calculation of U'_0 it is more convenient to deal with the heat of reaction (at any temperature T) at constant pressure, *viz.* Q'_p. This quantity is simply (U′ + RT), since in the above case 2 moles of I (atomic iodine) are formed from 1 mole of I_2, the external work being therefore RT.

[1] G. Starck and Max Bodenstein, *Zeit. Elektrochem.*, 16, 961, 1910.

The expression Q'_p can be expressed as Q'_0 or U'_0 + a series of ascending powers of T, each coefficient being determined from the molecular heats at constant pressure of the reactants and resultants, and hence U'_0 can be calculated. On our notation we have written for a gaseous reaction—

$$U' = U'_0 + \alpha'T + \beta'T^2.$$

Hence from the equation $Q'_p = U' + \Sigma\nu RT$ we get—

$$Q'_p = U'_0 + \alpha'T + \beta'T^2 + \ldots + \Sigma\nu RT = U'_0 + (\alpha' + \Sigma\nu R)T + \beta'T^2 +, \text{ etc.}$$

and

$$\frac{\partial Q'_p}{\partial T} = \alpha' + \Sigma\nu R + 2\beta'T +, \text{ etc.}$$

Now the molecular heat at constant pressure of any monatomic gas (I) at *any* temperature is 5 calories per degree. Also the molecular heat of iodine (molecular) I_2, is shown by experiment to be given by the expression—

$$H_p = 6{\cdot}5 + 0{\cdot}0038T.$$

Hence the molecular heat at constant pressure of reactants − molecular heat of resultants which we may denote by

$$\Sigma\nu H_p = (6{\cdot}5 + 0{\cdot}0038T) - 2 \times 5 = -3{\cdot}5 + 0{\cdot}0038T.$$

Near zero the value of $\Sigma\nu H = \alpha' + \Sigma\nu R$.

But in the neighbourhood of absolute zero—

$$\Sigma\nu H_p = 6{\cdot}5 - 10 = -3{\cdot}5.$$

$$\therefore \alpha' + \Sigma\nu R = -3{\cdot}5.$$

Now we have—

$$\Sigma\nu H_p = \frac{\partial Q'_p}{T} = \alpha' + \Sigma\nu R + 2\beta'T.$$

$$\therefore -3{\cdot}5 + 0{\cdot}0038T = -3{\cdot}5 + 2\beta'T.$$

$$\therefore \beta' = 0{\cdot}0019.$$

It should be mentioned that the value employed for $\Sigma\nu C_0$ is one which happens to fit the equation (at least at one temperature). The total expression, however, as is seen from the above table, holds over the entire range investigated and in all probability over any range whatsoever (as long as the term containing γ' can be neglected). Having thus obtained the information that $\Sigma\nu C_0$, that is $2 \times C_{0_I} - C_{0_{I_2}} = +0{\cdot}422$, Bodenstein has calculated the value of C_{0_I}, using the known value $+4{\cdot}0$ for $C_{0_{I_2}}$. C_{0_I} thus comes out to be $2{\cdot}2$. Bodenstein points out that this is the first instance in which the chemical constant for a monatomic substance has been *accurately* obtained.

Modification of the Equation for Homogeneous Gaseous Equilibria.

As we have seen, the terms containing β' and γ' can be in general neglected. Also the value of U'_0 is very nearly equal to the heat developed at *ordinary* temperatures and under constant pressure (this being

the quantity for which experimental data can most conveniently be obtained).[1] Equation (9c) can therefore be written in the following approximate, but at the same time useful, form—

$$\log_{10} K_p = \frac{Q'_p}{4{\cdot}571T} + \Sigma\nu 1{\cdot}75 \log_{10} T + \Sigma\nu C_0.$$

For examples of the use of this formula, *cf.* O. Brill, *Zeitsch. physik. Chem.*, **57**, 721, 1907.

Application of Nernst's Theorem to the Calculation of Equilibria in Heterogeneous Systems (Gas—Solid, or Gas—Liquid).

Let us take as a typical instance the dissociation of calcium carbonate, *viz.*—

$$CaCO_3 = CaO + CO_2.$$

The isotherm for the affinity A of the above reaction when all components are in the solid state is—

$$A = RT \log K - RT\Sigma\nu \log C$$

where $K = \frac{C_{\epsilon CaO} \times C_{\epsilon CO_2}}{C_{\epsilon CaCO_3}}$, and C in the last term refers to saturation concentration of the vapours.

The two terms $C_{\epsilon CaO}$ and $C_{\epsilon CaCO_3}$ are, however, simply constant concentrations, since the lime and calcium carbonate are present in the solid form. The isotherm may thus be written—

$$A = RT \log C_{\epsilon CO_2} - RT \log C_{\text{saturated } CO_2}.$$

The term $\Sigma\nu i$ in the vapour pressure expression (equation (6A)) becomes simply i for CO_2 alone, and the equation becomes identical with equation (6) itself. Hence in the final expression (equations (9), (9A), (9B), or (9C)) the expression $\Sigma\nu C_0$ is simply the value of C_0 for 1 mole of CO_2 gas. This is taken by Brill (*loc. cit.*) to be 3·2. The term $\log K_p$ becomes identical with $\log p$, where p is the equilibrium pressure of CO_2 in the presence of CaO and $CaCO_3$. For such heterogeneous equilibrium the approximate form of equation (9c) may be used, *viz.*—

$$\log_{10} K_p = \frac{Q'_p}{4{\cdot}571T} + \Sigma\nu 1{\cdot}75 \log_{10} T + \Sigma\nu C_0.$$

On substituting the equivalents for these terms given above, one finds finally for the dissociation equilibrium of *any* carbonate the expression—

$$\log_{10} K_p = \frac{Q'_p}{4{\cdot}571T} + 1{\cdot}75 \log T + 3{\cdot}2.$$

Q'_p denotes the heat of dissociation of the carbonate investigated. Since such dissociation increases with increasing temperature, the term Q'_p is heat absorbed and must therefore be taken with a negative sign.

[1] The value of U'_0 used for the $2HCl \rightarrow H_2 + Cl_2$ reaction is really this quantity.

The following table (*cf.* Brill, *loc. cit.*, p. 736) contains the values of T_1 (calculated and observed) when the dissociation pressure $p = 1$ atmosphere. In this case $\log_{10} p = 0$, and hence—

$$\frac{-Q'_p}{4{\cdot}571\,T_1} = 1{\cdot}75 \log_{10} T_1 + 3{\cdot}2.$$

Substance.	Q'_p Observed by Thomsen.	T_1 Observed.	T Calculated.	Observer.
$AgCO_3$.	− 20,060	498°	548°	Joulin
$PbCO_3$.	− 22,580	575°	610°	Colson
$MnCO_3$.	− 23,500 (Berthelot)	600°	632°	Joulin
$CaCO_3$.	− 42,520	1098°	1091°	Brill
$SrCO_3$ . .	− 55,770	1428°	1403°	Brill

Several other illustrations of the applicability of the theorem to heterogeneous systems in which gases are present are cited by Nernst (*Applications of Thermodynamics to Chemistry*, p. 96, *seq.*). In the present instance we shall discuss only one further problem, which is of great importance, namely, *the calculation of the electromotive force of a gas cell from purely thermal data*. To apply the theorem to such a system, which is not an entirely condensed one, we have to proceed in principle as follows (quotation from Nernst, *Sitzungsber. Berliner Akad.*, p. 255, 1909): "We think of the cell at a temperature so low that the gases become either liquid or solid, and apply our theorem to this state. We then take into consideration the equilibrium between the solid or liquid substances and their vapours and thence by applying the Second Law of Thermodynamics we can carry out calculations for any temperature and pressure." In this way we can realise the conditions obtaining in an actual gas cell. A typical illustration is the Knallgas cell, in which the reaction—

$$\underset{\text{gas}}{2H_2} + \underset{\text{gas}}{O_2} \rightarrow \underset{\text{liquid}}{2H_2O}$$

goes on and yields the electromotive force. In this reaction the equilibrium constant in the homogeneous phase is given by—

$$K = \frac{C^2_{\epsilon H_2O}}{C^2_{\epsilon H_2} \times C_{\epsilon O_2}}.$$

If the reaction were made to take place under such circumstances that all the substances were pure liquids or solids, the affinity A of the reaction is given by (*i.e.* the affinity of formation of 2 moles of H_2O)—

$$A = RT \log K - RT\Sigma\nu \log C_{\text{saturated}}.$$

Now exactly as in the case of the dissociation of the carbonates, the term for the concentration of saturated water vapour present in both of the above terms cancels. The term $\Sigma\nu \log C$ may therefore be taken as equivalent to—

$$-(2 \log \underset{\substack{\text{Saturated vapour}\\ \text{over liquid hydrogen.}}}{C_{H_2}} + \log \underset{\substack{\text{Saturated vapour}\\ \text{over liquid hydrogen.}}}{C_{O_2}}).$$

[N.B.—The negative sign comes into the above expression since the terms for H_2 and O_2 occur in the denominator of the original expression for K.] Passing to partial pressure terms, and still omitting the term for water vapour, we see that—

$$\log K_p = \log \left(\frac{1}{\underset{\text{Equilibrium pressure.}}{p^2_{\epsilon H_2}} \times \underset{\text{Equilibrium pressure.}}{p_{\epsilon O_2}}} \right) = - (2 \log \underset{\text{Equilibrium pressure.}}{p_{\epsilon H_2}} + \log \underset{\text{Equilibrium pressure.}}{p_{\epsilon O_2}}).$$

Proceeding as before we reach equations (9), (9A), (9B), or (9C). In these $\Sigma\nu C_0 = \{C_0$ for resultants $- C_0$ for reactants$\}$; and as the resultant H_2O term is dropped, since it occurs in both terms in the expression for A, it follows that—

$$\Sigma\nu C_0 = - (2C_{0H_2} + C_{0O_2}) = - 7{\cdot}2.$$

One should observe that the term $\Sigma\nu$ in the above case has the value $- 3$, since it must always represent number of molecules of resultants $-$ number of molecules of reactants. $\Sigma\nu$ becomes in this case simply the number of molecules of reactants taking part, *viz.* $(2H_2 + O_2)$. The term $\Sigma\nu 1{\cdot}75 \log_{10} T$ in equation (9C) becomes now $- 3 \times 1{\cdot}75 \log_{10} T$, or $- 5{\cdot}25 \log_{10} T$. The term U'_0, *i.e.* total energy change in formation of 2 moles of liquid water in this case, has been found, from direct measurements of heat of formation of liquid water from the gases hydrogen and oxygen at constant pressure at several temperatures, to be 137,400 calories. In the *formation* of water, heat is evolved, that is, the total energy decreases and hence U'_0 appears with a positive sign. Equation (9C) can thus be written—

$$\log_{10} \frac{1}{p^2_{\epsilon H_2} \times p_{\epsilon O_2}}$$

$$= \log_{10} K_p = \frac{137400}{4{\cdot}571T} - 5{\cdot}25 \log_{10} T + 0{\cdot}010T - 7{\cdot}2$$

from which $\log_{10} K_p$ can be calculated.

Now the affinity A of the reaction $2H_2 + O_2 \rightarrow 2H_2O$, in which the reactants are gaseous and the resultant a liquid, *i.e.* the affinity of the actual process occurring in the Knallgas cell, is given by—

$$A = RT \log \frac{1}{p^2_{\epsilon H_2} \times p_{\epsilon O_2}} - RT \log \frac{1}{p^2_{H_2} \times p_{O_2}}$$

where the term p_{H_2O} has been eliminated. If the oxygen and hydrogen are supplied to the cell, both at 1 atmosphere pressure, the above expression reduces to—

$$A = RT \log \frac{1}{p^2_{\epsilon H_2} \times p_{\epsilon O_2}} - RT \log 1 = RT \log \frac{1}{p^2_{\epsilon H_2} \times p_{\epsilon O_2}}.$$

This can be calculated numerically from equation (9C) given above. We can thus calculate the affinity of the reaction in the Knallgas cell. Now A refers to the formation of 2 moles of water. To form 2 moles of water electrically requires four faradays, and hence $A = 4E$, where E is the electromotive force of the cell. Calculating K_p as above

for the temperature 290° absolute, and obtaining the numerical value of A from this, and hence the numerical value of E, one obtains *from purely thermal data, by the aid of Nernst's Theorem*, that—

$$E_{290° \text{ abs.}} = 1{\cdot}242 \text{ volts.}$$

We have now to compare this value with the observed. Direct observation of the electromotive force of this cell has shown $E_{290° \text{ abs.}}$ to be 1·15 volts, but as already pointed out this is certainly too low owing to the difficulty of saturating the platinum electrode with oxygen. On applying the principle of virtual work, the expression obtained for the e.m.f. of this cell is—

$$E = \frac{RT}{4} \log_e \frac{1}{\pi_{H_2}^2 \times \pi_{O_2}}$$

where π_{H_2} and π_{O_2} denote the partial pressures of hydrogen and oxygen at the temperature T in saturated water vapour.[1] At fairly high temperatures the degree of dissociation of water vapour has been experimentally obtained, and by simply using the isochore expression in its integrated form containing the constant I, which is determined from a directly obtained value of K_p (*no* use being made of the Nernst Theorem), one finds that at 290° abs. the value of—

$$\pi_{H_2} = 0{\cdot}0191 \times 1{\cdot}80 \times 10^{-27} \text{ atmospheres}$$

and

$$\pi_{O_2} = \frac{0{\cdot}0191 \times 1{\cdot}80 \times 10^{-27}}{2} \quad ,,$$

whence $E_{290° \text{ abs.}} = 1{\cdot}232$ volts (Nernst and von Wartenberg, *Zeitsch. physik. Chem.*, **56**, 544, 1906). Other values are E = 1·224 (G. N. Lewis, *Zeitsch. physik. Chem.*, **55**, 449, 1906); and E = 1·234 (Brönsted, *Zeitsch. physik. Chem.*, **65**, 744, 1909). This may be regarded as the true "observed" value for the electromotive force of the

[1] In the cell H_2 | electrolyte | O_2, if p_{H_2} and p_{O_2} represent the (arbitrarily chosen) partial pressures of the gas electrodes, and p_{H_2O} is the vapour pressure of undissociated water, then if the formation of 2 moles of water took place as vapour only, the work A would be—

$$A = RT \log K_p - RT\Sigma\nu \log p$$

$$= RT \log \frac{p_{eH_2O}^2}{p_{eH_2}^2 \times p_{eO_2}} - RT \log \frac{p_{H_2O}^2}{p_{H_2}^2 \times p_{O_2}}.$$

Since in the presence of liquid water $p_{eH_2O} = p_{H_2O}$ we can write—

$$A = RT \log \frac{1}{p_{eH_2}^2 \times p_{eO_2}} - RT \log \frac{1}{p_{H_2}^2 \times p_{O_2}}.$$

Also if we use the symbols π_{H_2} for p_{eH_2} and π_{O_2} for p_{eO_2}, and also feed in the gases at the electrodes at 1 *atmosphere* pressure, then

$$A = RT \log \frac{1}{\pi_{H_2}^2 \times \pi_{O_2}}$$

and since the formation of two moles of water from the *ionic* state would require 4 unit charges (faradays), it follows that—

$$E = \frac{A}{4} = \frac{RT}{4} \log \frac{1}{\pi_{H_2}^2 \times \pi_{O_2}}.$$

Knallgas cell, and it is clear that this agrees pretty well with that calculated by the aid of the Nernst Theorem, *viz.* $E_{290°} = 1{\cdot}242$ volts.

The discrepancy which does exist is discussed by Nernst (*loc. cit.*). It is due to the abnormal behaviour of liquid water in respect of its molecular heat. By working with the data for ice, Nernst finds that at 0° (*i.e.* the temperature at which water and ice are in equilibrium under 1 atmosphere pressure), the electromotive force of the cell calculated from purely thermal data should be 1·2393 volts. To find the value of this at 290° abs. we can simply use the Gibbs-Helmholtz equation directly, *viz.*—

$$E_{273° \text{ abs.}} - \frac{Q}{23046} = 273\frac{dE}{dt}$$

whence

$$\frac{dE}{dt} = -0{\cdot}00085.$$

Using this value for $\frac{dE}{dt}$, one finds that—

$$E_{290°} = 1{\cdot}225 \text{ volts}$$

a quantity which agrees very well with the "observed" value.

The Nernst Theorem can thus be satisfactorily applied to the reactions taking place in gas cells.[1] The following table contains the values obtained with a few gas cells:—

Reaction.	Temperature.	E Observed.	E Calculated.
$2H_2 + O_2 \rightarrow 2H_2O$	290°	*1·232*	1·225
$2Ag + Cl_2 \rightarrow 2AgCl$	290°	1·157	1·092
$Pb + Cl_2 \rightarrow PbCl_2$	290°	1·612	1·594
$H_2 + Cl_2 \rightarrow 2HCl$ 6 normal solution .	303°	1·160	1·170
$H_2 + Cl_2 \rightarrow 2HCl$ 1 „ „ .	298°	1·366	1·365

We have already referred to the somewhat analogous problem of the electromotive force of cells in which the reaction takes place in *solution*. This is to be distinguished from reactions occurring between *pure* condensed substances (*i.e.* each phase consisting of a single chemical entity). To the latter we have already seen that the theorem of Nernst can be most directly applied. For the case of solutions we can proceed by the help of the artifice already exemplified in the case of the Clark cell, *i.e.* calculating the electromotive force at such temperatures that solid phases are present, and then with the aid of subsidiary data, *e.g.* solubility temperature curves, calculate what the electromotive force would be for the actual temperature in question.

[1]For further details in connection with the question of cells, *cf.* Nernst, *Sitzungsber. Berlin. Akad.*, 1909.

CHAPTER XIV.

Behaviour of systems (in equilibrium and not in equilibrium) exposed to radiation—Photochemistry—Thermodynamical treatment of photochemical reactions.

In this chapter a brief account is given of the behaviour of material systems under the influence of radiation, which behaviour, when the radiation consists of short waves (visible or ultra-violet), is included in the term *Photochemistry*.[1] As a matter of fact, however, recent advances, due notably to Trautz and Krüger, have emphasised the importance of long wave radiation as the possible origin of "ordinary" or thermal reactions, so that it will be evident that radiation in general is of fundamental significance from the chemical standpoint. Radiation chemistry has been developed by the aid of the ordinary kinetic theory and by thermodynamics, but in addition to these two modes of investigation a third mode, expressed in the *quantum theory* of Planck, has within recent years proved of service. This chapter will be devoted to the survey of *Photochemistry* along what may be now regarded as classic lines. In Vol. III. the concept of the unitary theory of radiant energy—the quantum theory—and some of its applications will be discussed.

The Source of Light Radiations.

On the basis of the electromagnetic theory of light, the vibrations of small charged particles called "radiators" or "vibrators," which may be either atoms themselves or electrons present in the molecules of all substances, produce electromagnetic waves of their own period, *i.e.* light waves of a given colour which are radiated off into space. The act of radiation of such waves represents, of course, a loss of energy on the part of the vibrating system, and the movement of the vibrators will be gradually damped down and cease unless energy is communicated to them. There are essentially two ways in which this energy supply may be kept up. First, the *temperature* of the body as a whole may be kept high. This means that the kinetic energy of the molecules is great, and the consequent energy interchange at collisions can go to keep the radiators in vibration. Note that no chemical change in the structure of the molecules is assumed. This type of radiation, which is kept up by purely physical means, is called *temperature radiation.* Any substance heated to a sufficiently high temperature must give rise to such

[1] *Cf.* the volume on *Photochemistry*, by H. S. Sheppard, in this series of text books. Further details may be obtained there.

temperature radiation. The higher the temperature the greater the collision frequency of the molecules, and consequently the more rapid and more energetic are the vibrations of the radiators inside the molecules. Rapid vibration means short wave length or large frequency, and as the temperature is raised evidently the radiations which corresponded at first to long waves, *i.e.* the infra-red, may be made to possess wave lengths corresponding to the visible spectrum range, and even the ultra-violet. Radiation represents energy, *i.e.* radiant energy. Temperature radiation consists theoretically of all frequencies or wave lengths between 0 and infinity. The distribution of energy between various regions is by no means equal. The distribution, in fact, exhibits a maximum at a certain range of frequencies, and the position of the maximum varies with the temperature of the radiating source. Radiators at ordinary temperatures do not emit visible light, because the energy of the radiation corresponding to the limits of the visible region is far too small to affect the eye. The higher the temperature of the source the greater the radiant energy throughout any given range of frequencies or wave lengths. Hence when a substance is raised to a sufficiently high temperature the radiation energy corresponding to the visible region becomes intense enough to affect the eye and the substance is said to emit light. Particles capable of vibrating so rapidly as this must necessarily possess very small mass, and it is generally considered that the radiators in such cases are electrons. If all the electrons had the same period, the light would be of a certain colour. If, as is generally the case, the periods cover a wide range, the total light emitted will be white, and on analysing by means of a prism a *continuous spectrum* will be obtained.

Besides this purely temperature radiation we have what is called *luminescence*. In this, which is generally present in incandescent vapours and gases (ordinary Bunsen burner), the supply of energy to the vibrating electrons comes from chemical change, *i.e.* intramolecular changes in the molecules themselves. There are several kinds of luminescence, covering, in fact, all possible sources of energy supply other than effects due to temperature. It must be noted that luminescence may be exhibited by systems whose temperature is low, and, in fact, it was observations on such that first showed the necessity of assuming that causes other than high temperature might be the origin of the visible light. Thus Pringsheim has obtained effects in a photographic plate from a CS_2 flame whose temperature was only 150° C. Pure temperature radiation would in this case (at 150° C.) have produced no photographic effect, for the temperature radiation—which must always be present even with luminescence—would correspond almost entirely to vibrations far in the infra-red.

We shall return again to the subject of temperature radiation and luminescence after considering some of the evidence which leads to the conclusion that it is a charged particle of dimensions much smaller than an atom, *i.e.* an electron, which gives out *visible* and ultra-violet rays by its vibration.

Suppose we have two electric charges of opposite sign, $+ e$ and $- e$, whose distance apart undergoes a periodic change of amplitude a, then according to Hertz (quoted in Drude's *Optics*, p. 530), the electromagnetic energy emitted in a half period is—

$$\frac{8\pi^4}{3\lambda^3}e^2a^2$$

where λ is the wave length of the radiation emitted. Hence the amount of energy radiated per second from such a charge is—

$$L = \tfrac{8}{3}\pi^4\frac{e^2a^2}{\lambda^3 T} \quad \text{or} \quad \tfrac{8}{3}\pi^4 c\frac{e^2a^2}{\lambda^4}$$

where T is the periodic time of a single complete vibration, or $\frac{1}{T}$ is the frequency of the radiation and c is its velocity (*i.e.* the velocity of light, namely, 3×10^{10} cms. per second), these terms being connected by the well-known relation—

$$c = \frac{\lambda}{T} = \nu\lambda$$

where ν is the frequency of vibration.

Now, for the particular case of incandescent sodium vapour, which happens to be mainly a luminescent source and only partly a temperature source, Wiedemann has shown that the energy emitted per second in the two D lines by 1 gram of sodium is 3210 gram-calories or $13{\cdot}45 \times 10^{10}$ ergs. The sodium vapour may be regarded as partially ionised; that is to say, a neutral atom has given off an electron (charge $- e$), the remainder, the positive ion, having the charge $+ e$. Suppose that the electron vibrates with respect to the positive ion, which latter happens to be much larger in mass and size, and may be regarded as at rest. Then from each atom of sodium vapour thus ionised we would expect to obtain the energy L per second. From Perrin's determination of the number of molecules in 1 gram-molecule, *viz.* 6×10^{23} (in round numbers), it is evident that there are 6×10^{23} atoms in 23 grams of sodium vapour, or $2{\cdot}6 \times 10^{22}$ atoms, in 1 gram. Since each ionised atom when radiating gives rise to a radiation energy L per second, then, if all the atoms were thus radiating, the energy emitted per second from 1 gram of sodium would be—

$$\tfrac{8}{3}\pi^4 c\frac{e^2a^2}{\lambda^4} \cdot 2{\cdot}6 \times 10^{22}.$$

This is evidently a maximum value, since ionisation is probably not complete. It may give the correct order of magnitude, however. Equating this to Wiedemann's experimental value, we obtain—

$$\tfrac{8}{3}\pi^4 c\frac{e^2a^2}{\lambda^4} \cdot 2{\cdot}6 \times 10^{22} = 13{\cdot}45 \times 10^{10}.$$

The quantity e, the unit charge, is approximately $4{\cdot}6 \times 10^{-10}$ electro-

static units (*cf.* Vol. I., Chap. I.). Further, the mean wave length of the D lines emitted by incandescent sodium vapour is 0·000589 cm. Hence for the amplitude of the vibrating particle, we obtain—

$$a = 8 \times 10^{-10} \text{ cm.}$$

The diameter of an atom is of the order 10^{-8} cm. The amplitude of the vibrating particle is thus considerably smaller than the diameter of an atom itself. It seems reasonable to assume, therefore, that the actual vibrating agent is an electron,[1] which is known to have the mass of only $\frac{1}{3000}$ of a sodium atom.

Radiation due to Temperature alone (as distinct from Luminescence).

There are several important relationships or laws which may be mentioned in connection with temperature radiation. Since, however, these form a part of physical optics, a brief statement must here suffice. For their deduction, or theoretical significance and practical applicability, a textbook on physical optics is to be consulted, *e.g.* Wood's *Physical Optics*.

Laws of Balfour Stewart and Kirchhoff.

The first Stewart-Kirchhoff Law states that light of any given wave length emitted by a (gaseous) body can also be absorbed by that body at a lower temperature. This law at once affords a reasonable explanation of the absorption lines—the Frauenhofer lines—in the sun's spectrum. The sun itself is at an intensely high temperature, and is surrounded by a gaseous atmosphere of similar constitution, but at a lower temperature. This atmosphere, which contains several metallic vapours, such as that of sodium, present in it, absorbs to a certain extent the sodium light given out by the sun itself, and hence the Frauenhofer *dark* lines corresponding exactly to the yellow D lines of incandescent sodium vapour. The Frauenhofer lines, with the aid of the above law, allow us to ascertain the chemical constitution of the sun. Of course, the light emitted by an incandescent vapour is by no means purely temperature radiation. Luminescence is likewise present. The Stewart-Kirchhoff Law, therefore, applies *in general*. The Stewart-Kirchhoff Second Law states that the ratio of the emissive power of the body to its absorptive power is a function of the temperature only, and is the same for all bodies emitting "temperature radiation". We can write this in the form $\frac{E}{A}$ = constant. By the term "emissive power" is meant the intensity of radiation of given wave length emitted at a given temperature. The absorptive power of a body is the fraction of incident radiation absorbed by the body. A *perfectly* absorbing or

[1] See F. A. Lindemann, *Verhl. d. Phys. Gesell.*, 13, 482, 1911, for an alternative method of treatment.

"black" body is one, as the name implies, for which A is unity. If the emissive power of a black body, at a given temperature is e, then since $A = 1$, $e = \frac{E}{A}$. In other words, the emissive power of a *black* body or "full radiator" is equal to the ratio of the emissive to the absorptive power of *any* body at the same temperature. It is to be remembered that this is only true of temperature radiation.

Stefan's Law for Total Radiation.

According to Stefan, the *total* amount of energy radiated from a body which is giving out a series of different wave lengths, *i.e.* an entire spectrum, such radiation being due to temperature *only*, is proportional to the fourth power of the absolute temperature of the body, *i.e.* $\propto T^4$. Stefan was led to this conclusion from a consideration of Tyndall's data upon the radiation from a platinum wire. The quantities of energy radiated per second at the temperatures 1200° C. and 525° C. respectively were measured and the ratio found to be 11·7. Stefan noticed that $\left(\frac{1200 + 273}{525 + 273}\right)^4$ was equal to 11·6. The law has been tested frequently since, and the very accurate work of Lummer and Pringsheim has shown its applicability over a wide range of temperature. (For details see Preston's *Heat*, latest edition, and the *Annalen der Physik* for more recent communications). If we regard the radiation of the sun as a pure temperature effect (which is only approximately true), bolometric measurements give the amount of energy radiated per second, and hence, by applying Stefan's Law, the temperature of the sun may be calculated. The result works out as 6200° absolute; this, however, is necessarily approximate only. Stefan's Law has been deduced by Boltzmann from thermodynamical considerations applied to radiation.

The following is a simple proof of the expression :—

Consider an enclosed space containing temperature radiation, that is radiation which is a function of temperature only. The temperature of the radiation is T. The presence of the radiation means the existence of energy of the raditional type, and we can treat the enclosed quantity of radiation, *i.e.* the enclosed space thermodynamically, just as we have treated a material system, such as a perfect gas. If u is the energy density of the radiation, *i.e.* the amount of radiation present per unit volume of the space, and V is the total volume of the space, then the total energy U of the space is given by uV. On the basis of the electromagnetic theory of light Maxwell showed that radiation will exert a pressure p which is related to the energy density u by the simple expression :—

$$p = (1/3)\, u.$$

Measurements of Lebedew and of Nichols and Hull have verified this expression. If the enclosed space be fitted with a movable piston work

would have to be done by an external agent in order to push the piston inwards against the pressure of the radiation. If the decrease in volume, due to the movement of the piston, be δV, the maximum work done by the external agent is $p\delta V = \frac{u}{3}\delta V$. If the change be carried out isothermally, the radiation energy density u, which by definition is a function of temperature only, will remain unchanged. The volume has decreased by the amount δV. Hence, applying the Gibbs-Helmholtz equation—

$$A - U = T(dA/dT)_v$$

where A = work done *by* the system $= -\frac{u}{3}\delta V$, U = decrease in internal energy due to the process, and therefore $-U$ = increase in internal energy $= -u\delta V$

$$(dA/dT)_v = \frac{d}{dT}\left(-\frac{u}{3}\delta V\right)$$

and therefore,

$$-\frac{u}{3}.\delta V - u.\delta V = -\frac{T}{3}.\left(\frac{du}{dT}\right)_v.\delta V$$

or

$$4u dT = T du.$$

On integrating this expression we obtain—

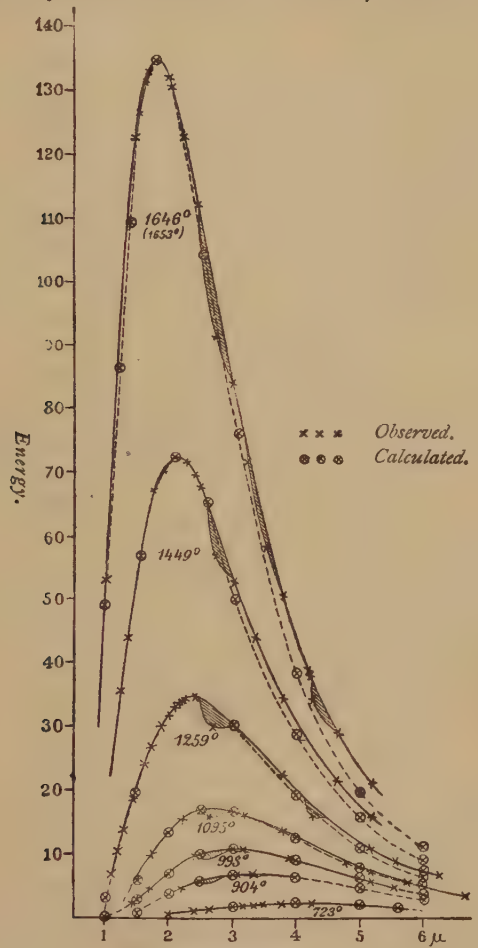
$$u = \text{constant} \times T^4.$$

The emissivity of a black body is proportional to the radiation density and hence the amount of energy radiated is proportional to the fourth power of the absolute temperature, which is Stefan's law for total radiation.

Wien's Displacement Law.

In Stefan's Law we only take account of the total energy emitted by a source. We now come to the much more complex question—complex even when we restrict ourselves to temperature radiation alone, and quite beyond our knowledge at present in the case of luminescence effects—namely, the distribution of the energy radiated among the various wave lengths emitted. Temperature radiation always gives rise to a *complete* spectrum. The energy from a source thus radiating is found to vary with the wave length emitted, but does not increase or decrease regularly as we pass along the spectrum. Instead, the energy-wave-length curve passes through a maximum at a certain wave-length region, the temperature of the source having a definite value (Fig. 53). By altering the temperature of the source, the *position* of the maximum is found to alter correspondingly. The direction of the change is such that the maximum shifts towards the *shorter* wave-length end of the spectrum as the temperature rises. This phenomenon of shift of maximum is taken account of in Wien's *Displacement Law*. If we denote by λ_{max} the wave length corresponding to the energy maximum, and by T the absolute temperature of the radiating black body, Wien's

law states that $\lambda_{max} \times T = \text{constant}$. Some of Lummer and Pringsheim's data in support of this are given in a subsequent table (the most recent and most thorough investigation up to 1914 upon the radiation from a black body is that of W. W. Coblentz, *Bull. Bur. Standards.*



(*From Sheppard's "Photochemistry".*)

FIG. 53.

Jan., 1914). Wien also deduced—by thermodynamic means—an important relationship between the maximum intensity and the absolute temperature. If we denote this intensity by E_{max}, Wien's relation is—

$$\frac{E_{max}}{T^5} = \text{constant.}$$

By E is meant the quantity of energy emitted per second from a given narrow wave-length region containing λ, the energy being absorbed by a thermopile or bolometer, and the amount of the energy, *i.e.* the magnitude of E, measured by the current produced as indicated by a very sensitive galvanometer. Some data in connection with this law are also included in the table. It may be mentioned that a totally absorbing or perfectly black body has been very nearly realised in practice by using a hollow blackened sphere or cylinder of metal (heated electrically) possessing a small opening through which the light passes and is reflected many times from side to side until it is practically all absorbed, for of course each reflection is accompanied by a considerable amount of absorption. It must be remembered, of course, that though we speak of radiation from a black body, the word "black" is not to be taken as referring to absence of colour. At high temperatures metals become "red" and finally "white" hot, though all the time they may be emitting temperature radiation only and functioning as "black" bodies. A better term is "full radiator". In Lummer and Pringsheim's experiments (*Annal. d. Physik*, **6**, 192, 1901) the spectrum was produced by refraction through a prism of fluorspar, which is very transparent, particularly to infra-red rays. As lenses could not be used, the image of the slit was formed by means of a concave mirror. A Lummer-Kurlbaum linear bolometer was employed to measure the radiant energy, the width of metal strip exposed being 0·6 mm. and the thickness 0·001 mm. The results were reduced to the normal spectrum, that is the spectrum produced by a grating, the constants for fluorspar having been previously determined by Paschen (*Annal. d. Physik*, **53**, 301, 1894). As the strip of platinum in the bolometer possesses *width*, the energy measured will not correspond to a single wave length, but to a small region lying between λ and $\lambda + d\lambda$. Also as the width of the slit is finite, the spectrum is not quite pure.

LUMMER AND PRINGSHEIM'S RESULTS.

Tabs.	λ_{max}, *i.e.* the Wave Length Corresponding to Maximum Radiation.	E_{max}, *i.e.* Maximum Intensity in Arbitrary Units.	$\lambda_{max} T$.	$\frac{E_{max}}{T^5} \times 10^{17}$.
621·2	4·53μ	2·026	2814	2190
908·0	3·28	13·66	2980	2208
1094·5	2·71	34·0	2966	2164
1259·0	2·35	68·8	2959	2176
1460·4	2·04	145·0	2979	2184
1646·0	1·78	270·6	2928	2246
		Mean of these and other data	2940	2188

The energy max. of the solar radiation lies in the yellow-green region, and by making use of the expression $\lambda_{max} T$ = constant, Langley calcu-

lated the temperature of the sun to be 5880° abs., which agrees fairly well with that calculated from Stefan's Law. It has been found that the relation $\lambda_{max}T$ = constant holds more accurately in general (for substances such as platinum, iron oxide, copper oxide, carbon, none of which are of course "perfectly black") than the other laws quoted. It is therefore of considerable practical applicability.

LAWS OF THE DISTRIBUTION OF ENERGY THROUGHOUT THE SPECTRUM.

We have already used the phrase "energy corresponding to a given wave length". This of course really refers to the energy emitted between the wave lengths λ and $\lambda + d\lambda$. It is impossible to isolate an actual single vibration experimentally. The method of procedure is to isolate a very small portion of the spectrum lying between two wave lengths very close together, and measure the energy. Several radiation formulæ dealing with the distribution of energy throughout the spectrum have been proposed. The most important of these are the formulæ of Rayleigh, of Wien, and of Planck. Rayleigh's formula is as follows—

$$E = \frac{ckT}{\lambda^4}$$

where c is the velocity of light *in vacuo*, k the gas constant per single molecule, *i.e.* $k = R/N$, where R is the gas constant per gram-molecule, and N is the number of molecules in one gram-molecule.

Wien's expression is—

$$E_\lambda = \frac{C}{\lambda^5} \cdot e^{-\frac{c'}{\lambda T}}$$

where C and c' are constants. The latter expression has been carefully investigated, notably by Lummer, Pringsheim, and Paschen, who have found that it holds with a great degree of accuracy over a wide region, but not over the entire region accessible to measurement. With very long waves and at high temperatures the expression ceases to accurately reproduce the experimental values of E_λ; Rayleigh's, on the other hand, holds in this region, but not in the short-wave region. These distribution laws mentioned are therefore not the last word on the subject. Yet another distribution law has been put forward by Planck, though the ideas lying at the base of this differ to such an extent from foregoing considerations, that a discussion of this expression must be postponed until we come to study Planck's revolutionary concepts regarding radiant energy, the so-called Quantum Theory (Vol. III.).

A point still remains to be mentioned in connection with temperature radiation. It must be remembered that the above expressions (Rayleigh's, Planck's, and Wien's) hold only for bodies emitting continuous spectra, *i.e.* ***all*** wave lengths. For line spectra, such as one finds in the case of incandescent gases and vapours, no relation has yet been found between λ and E. Pflüger has shown by bolometric measurements in the case of line spectra, that the largest deflections were obtained in the ultra-violet, *i.e.* the ultra-violet lines are "hotter"

than the infra-red. This is in direct opposition to the energy distribution in a continuous spectrum (due to temperature radiation).

NOTE.—The various laws which have here been very briefly discussed, are much more fully dealt with in Preston's *Heat* (Cotter's edition) and also by Wien, Lummer, Pringsheim, and Rubens, in vol. 2 of the *Reports of the International Congress of Physics*, Paris, 1900.

LUMINESCENCE.

This term is given to radiation of light waves, the vibrating electrons being kept in motion by processes dependent on factors other than temperature alone.[1] There are various kinds of luminescence, as the table given below will make clear.

These various types of luminescence may be very briefly described.

By fluorescence is meant the phenomenon of giving out light when under the influence of a beam, this emitted light differing in wave length from that causing the fluorescence. When the exposure to the beam ceases, fluorescence also ceases, and differs in this from phosphorescence, which is the continued emission of light after the external radiation is cut off. There are many fluorescent substances, *e.g.* calcium fluoride, uranium glass, liquids like petroleum, solutions of eosin, quinine sulphate, and many organic dyestuffs, such as litmus, in general. Wood has also found that the vapours of iodine, sodium, and mercury fluoresce. A law due to Stokes states that in fluorescence the wave length of the emitted light is always longer than the incident light. Thus ultra-violet light can be absorbed by several of the substances above-named, and given out as blue-green fluorescence. Apparent exceptions are Magdala red dye, chlorophyll, eosin and sodium vapour (the latter giving out a yellow-green fluorescence when stimulated by yellow light) :—

Source or Origin of the Radiation.	Name given to the Radiation.
1. Radiation caused by exposure of the body to external radiation.	*Photoluminescence*, which is divided into :— (*a*) Fluorescence. (*b*) Phosphorescence.
2. Gentle heating (*not* to a sufficiently high temperature to give temperature radiations of short enough wave length to be visible (the latter requires at least 360° C.)).	*Thermoluminescence.*
3. Friction or crystallisation.	*Triboluminescence.*
4. Chemical reactions.	*Chemiluminescence.*
5. Electrical charge or discharge.	*Electroluminescence*

[1] If the total radiation from a body is greater than that given by Stefan's Law, then the body must be emitting light by luminescence as well as the necessary temperature radiation.

Phosphorescence is shown by phosphorus, the sulphides of the alkaline earths, diamond, and several varieties of calcium fluoride. It is also exhibited by decomposing organic matter, though this perhaps should come under the heading of chemiluminescence. The Stokes Law for fluorescence also holds for phosphorescence. A very important point has been brought out in connection with the phenomenon of phosphorescence, namely, that impure substances are much more active than pure. Thus an addition of 0·00008 parts of CuO to 1 part CaO gives a very bright phosphorescence. In general we might say that mixed crystals, *i.e.* solid solutions, are good phosphorescent or fluorescent substances. In fact, the property of fluorescing in a vacuum tube while the discharge is passing, is taken to be evidence that the substance in question is a mixed crystal. We are indebted chiefly to Lenard and his pupils, as well as to Urbain, for our knowledge of this phenomenon.

As regards thermoluminescence there is little to be said. Certain substances on being gently warmed give out light waves. This, however, only happens if the substance has previously been exposed to light. The sulphides of the alkaline earths exhibit this phenomenon, which is evidently closely related to the property of phosphorescence.

Triboluminescence and crystalloluminescence are exhibited by many ordinary substances. Sugar crystals, for example, when crushed in the dark, emit light. The same is the case with crystals of uranium nitrate. The process of solidification of a melted substance is also in some cases (*e.g.* fused silver) accompanied by light emission.

Chemiluminescence is a phenomenon which is fairly general in chemical processes. Trautz (*Zeitsch. Elektrochem.*, **14**, 453, 1908) gives several instances: the precipitation of sodium chloride from solution by means of hydrochloric acid; the dissolution of solid sodium hydrate in hydrochloric acid; the reactions involving the evolution or absorption of gases, chiefly oxygen, as in the case of pyrogallol shaken with air, and formaldehyde with hydrogen-peroxide; as well as the complex oxidations which go on during putrefaction. Luminescence also occurs in the interaction of oxygen with phosphorus trioxide, with alkalies and alkaline earths, as well as by the interaction of halogens with these metals. Besides these heterogeneous reactions, light effects have been observed in homogeneous gaseous systems. Thus when a rapid stream of acetylene mixed with bromine vapour passes into a cylinder, a feeble green flame can be observed the temperature of which is very low. "Cold" flames in general are instances of chemiluminescence. Trautz sums up the characteristics of this phenomenon as follows: Chemiluminescence is very general. Its intensity increases (*cet. par.*) (1) with the heat effect of the reaction involved, (2) with the velocity of the reaction, and (3) enormously with rise of temperature. The colour of the luminescence is dependent on the reacting system, but is independent of the reaction velocity and of the temperature.

Electroluminescence is a familiar phenomenon since the introduction of the Geissler tubes for making gases incandescent for spectro-

scopic purposes. It has been observed that the luminescence in some cases continues for a short time after the discharge has ceased, as in the case of phosphorescence. The luminescence emitted by bodies (generally solids) when placed in a vacuum tube under the action of cathode rays, to which reference has already been made under fluorescence, may also be regarded as electroluminescence effects, as may also be the effects on a zinc sulphide screen when bombarded by X-rays, or radioactive α and β particles.

We have now discussed the problem of the different methods of light production. Under the next heading we shall deal with photochemistry proper, *i.e.* the study of chemical effects brought about in systems exposed to radiation.

Photochemistry.

General (*cf.* R. Luther (*Zeitsch. Elektrochem.*, **14**, 445, 1908)).—Reactions which are either initiated or accelerated by radiant energy, the wave length of which corresponds either to the visible spectrum or to the ultra-violet, are termed photochemical reactions. Such reactions are probably much more general than is usually believed. Perhaps the most familiar instances are the effect of light on silver salts, a reaction which is the basis of photography, and the effect of light on the chlorophyll of a plant leaf, which enables the plant to absorb oxygen, carbon dioxide, and water, and use these to build up the complex organic substances which are found in plants. It is rather an arbitrary distinction, of course, to limit photochemical reactions to the waves of the visible spectrum and the ultra-violet region, for infra-red waves also represent radiant energy, though their influence is usually regarded as belonging to heat effects. The wave-length limits for photochemical changes are therefore $800\mu\mu$ (red) to *circa* 300 or less (ultra-violet). As a rule, the shorter wave lengths, *i.e.* the ultra-violet region, are much more chemically active than the visible region. The generalisation which is at the base of photochemistry is, *that only those waves which are absorbed by the substance can be chemically active.* This was first stated by Theodor von Grotthus more than a century ago. That no simple connection exists between absorption and chemical action is at once shown by the fact that many cases are known where a strong light absorption corresponds to practically no detectable chemical reaction, and on the other hand a marked chemical action takes place in cases where absorption is apparently slight. The expression known as Beer's Law (1852) of light absorption depends essentially on the validity of the assumption that absorption is due to the *number* of individuals in a given layer, each acting *per se*. Thus if a solution is diluted to twice its volume and 2 cms. of this latter solution absorb to the same extent as 1 cm. of the original solution, the substance obeys Beer's Law. This principle may be expressed in the form—

$$I = I_0 e^{-kcd}$$

where I_0 is the initial intensity of the light, I is the intensity after passage through a layer of d cms., the concentration of the absorbing substance being c, and k the absorption constant (coefficient). If we take two substances at two concentrations c_1 and c_2, and if d_1 and d_2 are so chosen that the ratio I to I_0 is the same in both, then—

$$c_1 : c_2 :: d_2 : d_1$$

Beer's Law, however, does not hold in all cases.

As exposure proceeds, it is found in general that the chemical actions produced thereby also proceed. Photographic plates become darker the longer the exposure. A striking phenomenon known as solarisation, however, has been observed, namely, that after long exposure to bright sunlight the image of the sun appears on the negative, *light* on a dark ground. Other instances of the reversal effect are known, but no satisfactory explanation has yet been offered. For details, *cf.* Sheppard and Mees' *Investigations on the Theory of the Photographic Process* (Longmans, Green & Co., 1907). Turning to the question of reaction *velocity* an important point arises, namely, what is the connection between velocity and the intensity of the light? It has been found, *ceteris paribus*, *the reaction velocity is directly proportional to the light intensity*. This, however, can scarcely be regarded as an absolutely accurate statement, for cases are known in which the reaction velocity increases more slowly than the light intensity when the latter is increased. At this stage we have to distinguish two light effects, *i.e.* two different ways in which the light may act. First, it may simply act as a catalysing agent. That is to say, it may simply accelerate a reaction which would of itself proceed slowly in the dark. It can also act as a negative catalyst. Secondly, the light may actually originate a reaction which would otherwise not go at all, or it may alter the course of a reaction, different end products being obtained according as to whether a given reaction is allowed to take place in the light or in the dark. Of course, optical catalytic effects may be superimposed on the latter case at the same time.

As regards the catalytic effect, we can formulate the process as follows :—

Suppose two substances A and B react with each other, then, according to the Law of Mass Action, the rate at which this reaction goes on in the dark is—

$$\propto [A]^a[B]^b$$

where a and b determine the order of the reaction.

If now the same reaction takes place in the light, we may write for a given constant light intensity the rate of the reaction as—

$$\propto [A]^\alpha[B]^\beta$$

where α and β determine the order of the reaction in the light. It is important to note *that a and b, etc., are as a rule not the same as* α *and* β, *etc.*; in other words, the order of a given reaction may not be the same in the presence of light as it is in the dark. It has been found, as a matter of fact, that the photochemical exponents α and β, etc., are

never greater than, are rarely equal to, and are usually less than the corresponding *a*, *b*, etc., terms. Thus in light hydriodic acid splits into hydrogen and iodine, *viz.* $HI \rightarrow H + I$, *i.e.* a monomolecular reaction, while in the dark the following takes place: $2HI \rightarrow H_2 + I_2$, *i.e.* a bimolecular action. The photo reaction is here a catalysed one. Under certain circumstances it has even been found that the photochemical exponent comes out zero, showing that the rate is independent of the concentration of the substance taking part. This, however, only holds for a certain concentration range. When the dark and light reactions are of the same nature (the case discussed above), and when the rate of the dark reaction is not negligible, compared to that in the light, it has been found that the total velocity may be written as a simple sum of both, *i.e.*—

$$\text{Total velocity} = k_1[A]^a[B]^b + k_2[A]^\alpha[B]^\beta.$$

If the intensity of the light is I, then in general—

$$\text{Total velocity} = k_1[A]^a[B]^b + k_2 I[A]^\alpha[B]^\beta.$$

Photochemical reactions, as a rule, have very small temperature coefficients. So far we have regarded the reaction as going to an end. Photochemical effects have also been observed in reactions in which an equilibrium exists and is measurable. This brings us to the phenomenon of *photochemical equilibrium*, or, as we shall call it more accurately later, "*photo-stationary state*". In such cases the light energy may oppose the chemical forces doing work against them, thereby giving rise to a stationary state, which differs from the equilibrium point in the dark. It is no longer simply a catalytic effect. The photochemical stationary state, however, differs fundamentally from the ordinary chemical, as one would expect, in that, while the latter represents a permanent state for all time, the photochemical equilibrium holds good only as long as the light energy remains constant. On withdrawal of the light, the reaction, if reversible, passes into the ordinary chemical equilibrium state. A notable instance of this is to be found in the transformation of dianthracene into anthracene, which has been investigated by Luther and Weigert, and which we shall discuss later.

A further peculiarity which has been noticed in connection with photochemistry is the so-called "period of induction," *i.e.* an initial period during which no reaction appears to take place, but at the conclusion of which the reaction progresses in a normal manner. This was first observed by Bunsen and Roscoe in the union of hydrogen and chlorine. It is really due to secondary effects either of a physical or chemical nature, and will be discussed later. We may now pass on to consider some of the more important photo-phenomena in detail.

Division of Photochemical Reactions into Groups.

We shall here follow in the main the division of the subject put forward by F. Weigert (*Ahrens Sammlung*, Bd. **17**, 1911), and based on thermodynamical grounds. According to a well-known principle of

thermodynamics, a reaction which takes place in a vessel shielded from all external influence proceeds in such a direction that the free energy of the system decreases, and the reaction will cease when the free energy is a minimum. This is the natural course of the reaction under purely chemical forces. Such a reaction, in which free energy is lost, may be called a reaction involving a free energy loss ; a decrease in free energy means that work has been or may be done. Now, when light falls upon a system it may act in two ways. It may cause the system to carry out an ordinary reaction, involving a decrease in free energy, *i.e.* the reaction may go in the "natural" way, or, on the other hand, the light may actually *oppose* the chemical forces and cause a natural reaction to be reversed, or may initiate a reaction opposed to the natural one. In such a case the free energy of the system, instead of decreasing, actually increases. This may be called a free energy conservation reaction, or a reaction involving an increase in free energy. This sort of reaction will proceed until the light energy is no longer able to overcome the opposing chemical forces which have increased owing to the increase in free energy, and a stationary state of the system ensues. This stationary state will depend on the intensity of the light, and only secondarily upon mass action, so that such a state is to be clearly distinguished from an ordinary "chemical equilibrium" which is controlled entirely by the principle of mass action. On removal of the light the reaction may reverse itself, and the system return to its original state. In the case of reactions involving gain of free energy, we have therefore the possibility of "reversibility". We will now restate the above division of photochemical reactions, and will then proceed to discuss some examples. Photochemical reactions may be divided into the following classes :—

I. *Photo-reactions involving a decrease in free energy.*

In these reactions the free energy at the end is less than at the beginning. This group may be further subdivided into—

(*a*) Reactions consisting of several consecutive reactions, the first of which is photosensitive, and the others depend on it in a purely chemical manner.

(*b*) Reactions in which the light acts as a catalyst or produces an actual catalyst which hastens the purely chemical photo-insensitive reaction between the substances in the system. This is an instance of photocatalytic reactions.

II. *Photo-reactions in which the free energy of the system is increased by the light.*

In these reactions the free energy at the stationary state is greater than at the beginning. This group consists of *true reversible reactions.* In these the photochemical reaction is simple (there are no consecutive reactions). When the light is withdrawn the "dark reaction" (or reaction taking place in the dark) simply retraverses the "light reaction" (or reaction under the influence of light). The classical example of a reaction of this type is the polymerisation of anthracene to dianthracene in the light and its depolymerisation in the dark. This type of reaction is to be clearly distinguished from *apparently reversible reactions.* In

these the reaction is complex, *i.e.* a photosensitive reaction and therewith one or more purely chemical (photoinsensitive) reactions. The return path in the dark *differs from that* followed by the system in the light, and the reaction is really irreversible and the free energy decreases, *i.e.* Class I.

Class I.—Reactions Involving a Free Energy Loss.

Group (*a*).—To this group belong the interesting examples of oxidation and reduction of organic compounds investigated by Ciamician and Silber. Under intense radiation it has been found for example that nitrobenzene in the presence of alcohol is reduced first to phenylhydroxylamine (which changes partly into p. amido-phenol) and finally to aniline. Similarly the nitrobenzene in the presence of benzaldehyde passes at first into nitrosobenzene, the benzaldehyde being simultaneously oxidised to benzoic acid.

An important class of substances belonging to this group are the *photochemical sensitisers* used in photography. The true photo-reaction is the reduction of the silver bromide or chloride to some subsalt, a quantity of halogen being set free. This reaction by itself, as a matter of fact, as Luther has shown, is a simple reversible process involving a gain of free energy, *i.e.* in the dark the halogen unites with the subsalt to give the original salt, this latter reaction being in the "natural" direction. When, however, the silver salt is imbedded in gelatine, as in a photographic plate, the colour change is observed to take place much more rapidly, and is now no longer reversible. The gelatine has reacted with the liberated halogen according to the equation—

$$2AgBr + \text{gelatine} + \text{light} \rightarrow Ag_2Br + \text{brominated gelatine}.$$

The gelatine is here the photochemical sensitiser. By the continuous removal of liberated bromine it has caused the silver salt to continue decomposing, and at the same time has caused the reaction to become irreversible. The same sort of *chemical* sensitisation effect comes in if some silver chloride is placed in benzene and exposed to light. The silver salt darkens, the benzene becoming chlorinated. On the other hand, if some silver chloride be placed in carbon tetrachloride and then exposed to light, the darkening is extremely slow, as the liberated halogen cannot react with the carbon tetrachloride. These instances of chemical sensitisation are to be distinguished from *physical* sensitisation, to be referred to later.

Group (*b*).—Photo-catalytic reactions.

In these reactions the light simply hastens a process which would take place naturally. This is the result of observation, as far as it goes, but it does not tell us anything about the mechanism of the hastening drocess. In an attempt to advance a little further in this direction Weigert (*Annal. d. Physik*, **24**, 246, 1907) has put forward the following suggestions. The accelerating effect brought about by the absorbed radiation is due in the first place to the formation of a substance, this primary reaction being a process involving a gain of free

energy, and the substance so formed catalyses the main reaction, which thus takes place in a purely chemical manner, *i.e.* in the natural direction corresponding to decrease of free energy. According to this view the main reaction is really *not* photosensitive at all, the true photo-reaction being the formation of the catalyst. Weigert suggests reasons for believing that, in a gaseous system at any rate, the catalyst is present as a heterogeneous aggregation much larger than molecular size, and the effects produced by these aggregates belong therefore to heterogeneous catalysis.

The classic photo-catalytic reaction is that of the union of hydrogen and chlorine to form hydrochloric acid, according to the reaction—

$$H_2 + Cl_2 \rightarrow 2HCl.$$

This reaction was first thoroughly investigated by Bunsen and Roscoe in 1855 (Ostwald's *Klassiker*, 34 and 38). It had, of course, been the subject of earlier work, the most important conclusion of such work being the statement known as the Grotthus-Draper Absorption Law, *viz.* only those rays are effective which are absorbed. Draper had also made the extremely interesting observation that chlorine which had been exposed to light had somewhat different properties from unexposed chlorine, in that the previously exposed chlorine reacted much more rapidly with

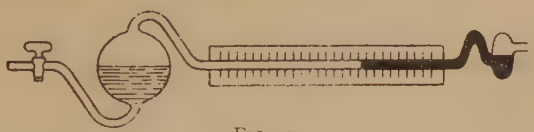


FIG. 54.

hydrogen (under the influence of light) than did the unexposed chlorine under the same conditions. Bunsen and Roscoe's first step consisted in the setting up of an accurate actinometer to measure the extent of the recombination of the gases under various conditions. This actinometer is shown in the figure (Fig. 54).

This gas mixture was confined over water (saturated with the hydrogen and chlorine), the water being screened from the light. When any hydrochloric acid was formed it dissolved in the water, and the meniscus in the horizontal capillary moved along a certain amount. The presence of water in the form of vapour is a factor of great importance in connection with the reaction discussed, for if the gases are very dry, then even in the presence of light combination only takes place slowly. The water molecules *may* therefore take part in the formation of the photochemical catalyst. Bunsen and Roscoe were the first investigators to fully study the phenomenon called the induction period, to which reference has already been made. In this connection it was observed that the sensitivity of the gaseous mixture increased slowly with time and reached a maximum in most cases after three to six days. This sensitivity or induction maximum decreased enormously if small quantities of oxygen were added, and at the same time the induction period is *shortened* by the oxygen so that with 1·3 per cent. oxygen

present in the mixture no period of induction is shown, but the reaction takes place steadily at a very slow rate. Also if the chlorine were previously exposed to light, Mellor has shown that the *induction period* may be very much shortened; the induction *maximum* or sensitivity of the gaseous mixture is, however, independent of the previous illumination. These observations suggest that chlorine by the absorption of chemically active rays is (partially) changed into an "active state"; but this goes only a very little way towards explaining the very complicated phenomena of induction period and induction maximum. The recent work of Burgess and Chapman (*Jour. Chem. Soc.*, **89**, 1402, 1906) points to the induction effects as being accidental and not really a characteristic of the photochemical process.[1] They have traced such effects to the presence of impurities, especially ammonia, in the water present or on the walls of the vessel. Thus by using a quartz vessel whose surface adsorbs gases and water vapour to only a slight extent compared with glass, and by employing carefully boiled out water, the induction period was made to entirely disappear. The phenomenon of "photochemical extinction," which was also discovered by Bunsen and Roscoe, is, according to Weigert, of rather doubtful significance, and may be no more characteristic of the actual photochemical process than is the induction effect. For a further discussion of such complications which belong to isolated instances, the reader is referred to Sheppard's *Photochemistry* (this series of textbooks). As an instance of an inorganic photo-catalytic reaction in solution, one may mention the oxidation of iodine ion in acid solution to the uncharged atomic or molecular state (Plotnikow, *Zeitsch. physik. Chem.*, **58**, 214, 1907). This reaction goes on of itself slowly in the dark. The light effect is therefore purely a catalytic one. The velocity is very dependent on the presence of other substances in the system, such as copper sulphate, quinine and acridine salts, chloroform, ether, and the nature of the acid used. Plotnikow also made the interesting observation that the blue and violet which are in this case the chemically active rays are only very slightly absorbed. Only a very small fraction of the radiant energy passing through the system is therefore used to form the catalyst. The reaction must therefore be a very sensitive one. It shows, as has already been pointed out, how impossible it is (at least at the present time) to connect chemical activity with magnitude of absorption.

Another instance of photo-catalysis in solution is the decomposition of aqueous sodium hypochlorite, according to the equation—

$$NaOCl \rightarrow NaCl + O$$

which proceeds according to the monomolecular law. One other instance of photo-reactions in solution may be mentioned, namely, the oxidation of oxalic acid in the presence of iron oxalate. The ferrous oxalate (which is red) oxidises itself to green ferric oxalate, according to the equation—

$$2Fe(C_2O_4) + H_2C_2O_4 + O \rightarrow Fe_2(C_2O_4)_3 + H_2O.$$

[1] The photochemical union of H_2 and Cl_2 has been further examined by Chapman and Whiston (*Trans. Chem. Soc.*, **115**, 1264 (1919)).

In sufficiently intense light this becomes red once more, the action being represented by—

$$Fe_2(C_2O_4)_3 + \text{light} \rightarrow 2Fe(C_2O_4) + 2CO_2.$$

The red ferrous oxalate is thus reformed, and the total reaction may be represented thus—

$$H_2C_2O_4 + O \rightarrow H_2O + 2CO_2.$$

The light in this case acts as a reducing agent on the ferri salt, the oxalic acid being at the same time oxidised.

Another reaction, the oxidation of sodium sulphite to sodium sulphate by atmospheric oxygen, is of interest because of the fact that it may be carried out thermally (that is, by infra-red radiation), and photochemically (by ultra-violet radiation). This reaction has been investigated by Mathews and Dewey (*Journ. Physical Chem.*, **17**, 211, (1913)) and by Mathews and Weeks (*Journ. Amer. Chem. Soc.*, **39**, 635, (1917)), particularly in connection with the effects of catalysts upon the photochemical change. In Vol. I. we have already briefly considered the effect of certain catalysts upon the thermal reaction. It is important to observe that a catalyst which is efficient under one set of conditions may be quite inactive under the other.

It is found that uranium salts act as positive catalysts for the photochemical reaction in proportion to their concentration. Some idea of the normal rate of reaction in Mathews' experiments in the absence of catalysts will be gathered from the fact that a 0·2N solution of sodium sulphite was oxidised completely by the light in less than three hours. One very remarkable discovery is that copper sulphate, which Titoff found to be a very strong positive catalyst for the thermal reaction, exerts no measurable effect upon the photochemical reaction. Pyridine strongly inhibited the photochemical change, when present to the extent of 5 c.c. to 1 liter of solution, whilst esters had a much weaker negative effect. Five drops of benzaldehyde to a liter of solution inhibited the reaction, whereas the same amount of glycerine had scarcely any negative effect. Bigelow had found that benzaldehyde and glycerine both acted as strong negative catalysts for the thermal reaction. Other substances examined, all of which exhibited a negative catalytic effect, were, urea (very feeble effect), phenol, quinine sulphate, and hydroquinone. In the presence of quinine sulphate and pyridine the solution acquires a green colour, and with hydroquinone it becomes opalescent when exposed to the light.

It is fairly evident that we have to do with selective absorption of light at certain regions of the spectrum. It is very necessary therefore to possess a complete knowledge of the absorption spectra of all the substances participating in the reaction. Mathews indicates that such measurements in the ultra-violet region are to be undertaken.

We have already had occasion to refer to the phenomenon of chemical sensitisation. Reference must also be made to a phenomenon known as *optical sensitisation*. This consists in making a system sensitive to a certain range of wave lengths by the addition of some foreign

substance (which does *not*, however, absorb chemically any of the products) to the system. Thus silver bromide on a plate is sensitive to the short wave-length region (violet and ultra-violet). It is only very slowly acted upon by the red. If, however, the silver salt is impregnated with some dyestuff, which absorbs the red, the plate is now sensitive to this colour. The optical sensitiser must absorb the wave length to which it is desired to make the silver salt sensitive. Many dyestuffs can be used for this purpose and they are characterised by the fact that they possess "anomalous refraction" in the region of the absorption band. For wave lengths slightly longer than those absorbed, such substances have an exceedingly great refractive index, and hence these act as very short wave lengths, to which the silver salt is itself sensitive. The use of orthochromatic plates depends on this effect. It appears as if we are here dealing with a resonance effect, the vibration of the electrons of the dyestuff, intensified by absorbing the light, causing vibrations of similar amplitude in the silver salt molecules. Besides the organic dyestuffs mentioned, it has been found that uranyl salts are also efficient optical sensitisers. All these substances fluoresce. This, however, is not an essential property. Thus Winther (*Zeitsch. Wissen. Phot.*, **7**, 409, 1909) showed that the light sensitivity of the Eder reaction, namely, the reduction of mercuric chloride to calomel by means of ammonium oxalate according to the equation—

$$2HgCl_2 + (NH_4)_2C_2O_4 = Hg_2Cl_2 + 2NH_4Cl + 2CO_2$$

which takes place readily in the presence of ferric salt when exposed to light, is due to the sensitivity of the non-fluorescing ferric ion. This latter is reduced in light to ferrous ion, and at the same time the oxalic acid is oxidised by the mercuric chloride. *How* this takes place is, of course, obscure.

Similar instances of catalytic optical sensitisation have been observed by Bruner (*Sitzber d. Krakau Ak. d. Wissen.*, 192, 1910). Maleic acid is transformed into fumaric acid in light, and this reaction is optically sensitised by bromine probably by the formation of intermediate compounds.

Let us now consider another well-known photo-catalytic chemical reaction, namely, the formation and decomposition of phosgene—

$$CO + Cl_2 \rightleftarrows COCl_2.$$

Of these three gases, chlorine is the only one which absorbs light (blue) in the visible region, and since this system has been examined in glass vessels (which exclude any ultra-violet), it can only be the chlorine which acts as or gives rise to the photo-catalyst. Working at 500° C. in presence of light, Weigert found that the speed in both directions was accelerated as one would expect if an ordinary chemical catalyst were in operation. It will be observed, however, that in the formation of phosgene, the catalysing source, namely, the chlorine, diminishes, while with dissociation of the phosgene the catalyst increases. Weigert looks upon the catalysis of the dissociation as an optical sensitisation whereby the chlorine, which absorbs the blue, makes the phosgene likewise

sensitive to this colour, although by itself it would only be sensitive to some of the much shorter ultra-violet wave lengths. In a similar manner Weigert has shown that chlorine can be used as an optical sensitiser for the union of oxygen with hydrogen to form water, oxygen with sulphur dioxide to form sulphur trioxide, and for the decomposition of ozone. These reactions will take place in the absence of chlorine under the action of ultra-violet light, but can also be made to take place even in the absence of such short wave lengths, if chlorine be present in the system to make the blue effective. The mechanism of such processes Weigert considers to be of the nature of a heterogeneous catalysis. "The chemical action of the light in such cases might be regarded as consisting first in the formation of nuclei in the exposed gases much in the same way as clouds are produced in supersaturated vapours. One may call these 'reaction nuclei,' and their effectiveness is of similar nature to that of any heterogeneous catalyst, in that the reacting substances are adsorbed in greater density on the surface, and in these places of higher concentration the reaction proceeds more rapidly in accordance with the principle of mass action." It will be observed that the reactants themselves are not assumed to be photochemically sensitive. In support of the above view one can cite the cloud formations in gases exposed to light, especially ultra-violet light, the quantitative course of many light reactions, and the possibility of "poisoning" by the addition of traces of certain foreign substances.

Photochemical After-effects.

It has been found that in some cases the reaction proceeds even after the withdrawal of the light. This phenomenon, which is called the photochemical after-effect, is thus roughly analogous to phosphorescence. One finds this effect in the photochemical decomposition of iodoform (Plotnikow); the transparent solution of iodoform in chloroform becomes brown owing to the presence of iodine, and even after light is withdrawn the deepening of colour continues for several days. Further, when a portion of a solution which has been exposed for a short time to the light is added to a quite fresh solution the latter begins also to decompose. According to Weigert, the assumption of heterogeneous nuclei formed by the light is sufficient to explain such after-effects in a very simple manner, for it is unlikely that such nuclei will break down immediately the light is withdrawn. To the same class of phenomena belongs that observed by Mellor, namely, that addition of exposed chlorine has the property of reducing or removing the induction period in the hydrogen and chlorine combination. Very definite after-effects have recently been obtained by Bruner (*Bull. de l'Ac. des Sciences de Cracovie*, 365, 1909) in the photobromination of toluene. The formation of the catalyst in this case is, however, dependent on the presence of oxygen since the effect cannot be observed with oxygen free solutions.

Apparently Reversible Reactions.

An example will make clear the meaning of this term. Let us take the case investigated by Luther and Plotnikow (*Zeitsch. physik. Chem.*, **61**, 513, 1908), namely, the oxidation of phosphorous acid H_3PO_3 by means of hydriodic acid and oxygen. We are here dealing with at least two consecutive reactions, the first of which is photochemically sensitive, the second not. The photo-sensitive reaction is the direct formation of iodine from the hydriodic acid according to the equation—

$$2HI + \tfrac{1}{2}O_2 = I_2 + H_2O.$$

This goes on slowly in the dark and rapidly in the light. The iodine thus produced is now used up by the phosphorous acid, to reform hydriodic acid and phosphoric acid, according to the equation—

$$H_3PO_3 + I_2 + H_2O \rightarrow H_3PO_4 + 2HI.$$

Under the action of light the system becomes brown, due to the formation of iodine (I_2). If the light is removed, the solution becomes colourless again, owing to the second reaction. On further exposure the brown colour is again developed, and may again be removed by the withdrawal of the light. This has all the appearance of reversibility, but is not so in reality, for gradually the phosphorous acid (H_3PO_3) in the system is being oxidised, and when this is complete the second reaction will no longer take place, *i.e.* finally a stage is reached at which the solution which has been coloured in the light is no longer discoloured in the dark. An end point has thus been reached, the total reaction being thus represented by—

$$H_3PO_3 + \tfrac{1}{2}O_2 = H_3PO_4.$$

The end point differs from the initial point, and the reaction has gone in the natural direction, *i.e.* the free energy at the end is less than at the beginning. The light has only acted, therefore, as a photo-catalyst, and the process does not really involve a gain of free energy at all. Such reactions belong, therefore, to the section already discussed of those in which the free energy decreases. It is only in true reversible reactions that the free energy may be made to increase by the action of the light.

Class II.—Reactions Involving a Gain of Free Energy.

True Reversible Reactions.

As already defined, these reactions retraverse in the dark exactly the same path they have traversed in the light. Under the action of the light a stationary state is reached as has already been discussed. It is of importance to ask the question, What will be the effect of a catalyst on this stationary state? If this were an ordinary chemical equilibrium, a simple catalyst should hasten both the direct and reverse reaction velocities to the same extent, leaving, therefore, the equilibrium point unchanged. The stationary state is, however, not brought about by

two opposed mass-action effects. On the one hand, there is a true mass-action effect, which will manifest itself by the system returning to the initial state if the light be removed. Opposed to this, when the light is on we have not a mass-action effect, but an optical effect of electromagnetic origin, so that the direct (optical) and reverse (mass action) reactions are of different origin, and hence one would not expect a catalyst to affect each in the same way. In other words, it is conceivable that the stationary state should be altered by the presence of a catalyst. We find an illustration of this in the photochemical decomposition of dry and wet carbon dioxide respectively. Thus under the action of ultra-violet light when the gas is absolutely dry, almost 50 per cent.[1] of the carbon dioxide is decomposed into carbon monoxide and oxygen (the oxygen being at the same time slightly ozonised). The stationary state here corresponds to very large dissociation, such dissociation being possible because, as Dixon has shown, the mass-action reunion of carbon monoxide and oxygen scarcely takes place at all when the gases are very dry. If, on the other hand, we start with moist carbon dioxide and expose it to light, practically no dissociation can be observed. In this case the water vapour, which is the catalyst, has a very great effect on the carbon monoxide-oxygen combination; so much so that the stationary state is shifted over quite to one side.

A good illustration of reversible photochemical reaction in the gaseous state is that of oxygen passing into ozone, the equilibrium being shifted by light. The ionisation of a gas by ultra-violet light is another illustration. Positive and negatively charged particles are produced in equal numbers, and on removing the light these recombine slowly.

Probably the most important photochemical reaction from a technical standpoint is that of the reduction of silver chloride or other silver salt. Luther has shown (*Zeitsch. physik. Chem.*, **30**, 628, 1899) that the pure salt *in the absence of gelatine or other foreign substance* decomposes in the light in the direction—

$$2AgCl \rightarrow Ag_2Cl + Cl$$

and on removal of the light the free chlorine reunites with the subsalt according to the equation—

$$Ag_2Cl + Cl \rightarrow AgCl.$$

To a given light intensity there corresponds a definite stationary state. In connection with this reaction it is of interest to mention the observation of Baker (*Jour. Chem. Soc.*, 782, 1892) that absolutely dry silver chloride in presence of light does not darken. Apparently here also a trace of water vapour acts as a catalyst. The alteration of the electrical properties of solid silver chloride, selenium, tellurium, under the action of light is also probably an instance of reversible photo-reaction, in which the free energy is increased by the light. Similarly, fluorescence and phosphorescence probably belong to the same group, but little is known in this direction. In these cases Waentig (*Zeitsch. physik. Chem.*,

[1] Chapman, Chadwick and Ramsbottom, *Jour. Chem. Soc.*, 91, 942, 1907.

51, 436, 1905) has suggested that under the action of light a new substance is formed (even in very small quantity) and this substance is retransformed into the original with emission of light. This view seems to be supported by the following observation on the effect of temperature upon fluorescence and phosphorescence made by Nichols and Meritt (*Phys. Rev.*, **18**, 355, 1904). It was found that on cooling to very low temperatures, fluorescent substances become phosphorescent, and substances which phosphoresce at ordinary temperatures no longer emit light. If we assume the above photochemical mechanism of the process one would expect the reaction to have a temperature coefficient, and hence the rapid change which at ordinary temperatures produces fluorescence would become slow at low temperatures and proceed even after the withdrawal of the incident light, *i.e.* fluorescence would become phosphorescence. Similarly, if a certain speed of reaction is necessary before any light can be emitted, it is conceivable that the slow phosphorescent reaction might become too slow at the lower temperature to emit any light at all.

The Photo-Decomposition of Water Vapour.

(*Cf.* A. Coehn, *Ber. d. Deutsch. Chem. Gesell.*, **33**, 880, 1910.)

On exposing a mixture of electrolytic gas (hydrogen and oxygen) to the action of ultra-violet light produced by a mercury lamp, Coehn showed in a very conclusive way that the gases combined (the temperature being about 150° C.) with one another "practically completely" to form water vapour. The extent of the combination was so great that no determinable quantity of either gas remained. Now, combination is the "natural" direction of the reaction, and can be brought about by local heating (*i.e.* by an electric spark). It might seem, therefore, that the light only acts as a catalyst of a reaction which would go of itself infinitely slowly. This conclusion is, however, not necessarily the correct one, and it is rendered still less certain by the behaviour of other gases, such as sulphur trioxide dissociating into sulphur dioxide and oxygen $SO_3 \rightleftarrows SO_2 + O$, in which the light was shown by Coehn actually to do work against the chemical forces. The only way to settle whether light can cause a reaction involving an increase in free energy in the system hydrogen, oxygen, and water vapour, is to find whether the light can shift the natural equilibrium point reached by the system in the dark. We may be able to decide whether this is the case or not by starting with the system H_2O vapour alone and exposing this to light. From the experiments of Nernst and von Wartenberg (*Zeitsch. physik. Chem.*, **56**, 543, 1906), it can be calculated that at 150° C. the quantity of hydrogen and oxygen in thermal or "dark" equilibrium with water vapour is only of the order 10^{-30} per cent.; that is to say, far below actual detection even by the most sensitive reagent. The action of light may be to cause this dissociation to increase, though at the same time it is evident that such photochemical action would have

to be very great before any appreciable quantity of either gas made its appearance. Even if negative results were obtained it would still leave the question undecided, since there might have been quite a considerable though still undetectable effect upon the equilibrium in such a case. Coehn investigated this problem in the following way: The water vapour was led in a slow, steady stream through a fine quartz tube close to the lamp (in fact, almost into the centre of the light source itself), and then finally into a eudiometer over mercury. The eudiometer allowed readings to be conveniently made down to 0·01 c.c. After only half an hour's exposure Coehn found 0·03-0·04 c.c. of gas produced, above the layer of condensed water vapour, which proved itself to be electrolytic gas by exploding completely under the action of a spark. Ultra-violet light, therefore, causes water vapour to dissociate to hydrogen and oxygen to an immensely greater degree than that produced by heat alone. Light must do work, therefore, against the chemical forces, and the photo-dissociation of water vapour is a process involving an increase in free energy. Coehn next proceeded to investigate the photochemical stationary state. By causing the vapour to pass through the apparatus at different speeds, Coehn found that with a rate slower than that in which 4·35 c.c. of liquid water per hour collected in the eudiometer, no further increase in electrolytic gas was produced. The quantity of gas actually produced in this limiting case was 0·88 c.c. Using the results of several experiments, the calculation of the degree of photochemical decomposition of water vapour (at 150° C.), when the system has reached the stationary state, showed that this is *at least* 0·2 per cent. This is about the same as the experiments of Nernst and von Wartenberg have shown to be the case for ordinary thermal dissociation in the neighbourhood of 2000° C. This photo-decomposition, as Coehn points out, is probably of considerable importance in meteorology, in connection with the behaviour of water vapour in the upper layers of the atmosphere.

Besides gaseous reactions, attempts have been made to find whether electrolytic dissociation is affected by light, but the results have turned out negative, due no doubt to the very great velocity of ionic reactions. As regards organic reactions which probably involve an increase in free energy, one may mention the transformation of maleic into fumaric acid, and cinnamic into α-truxillic, and, above all, the polymerisation of anthracene to dianthracene in light (the depolymerisation taking place in the dark), investigated very carefully by Luther and Weigert. This latter reaction has been used as the basis for extensive theoretical treatment, and this will be dealt with later.

There are, of course, many other photo-reactions in the domain of organic chemistry, but they are, as a rule, complex, and in such cases it is either difficult or impossible to determine whether the free energy increases or decreases. One important instance of complex reactions in which the free energy is increased merits a more detailed description, on account of the part it plays in biology, namely, the *assimilation of carbon dioxide by plants.*

This consists essentially in the transformation of the system ($CO_2 + H_2O$), which has very little free energy, into the system (Starch + O_2), which has a great deal of energy. The *total energy* difference (*not* the free energy difference) is practically that corresponding to the heat of combustion of the starch and amounts to 685 calories per formula weight ($C_6H_{10}O_5$). The possibility of this reaction occurring is intimately connected with the presence of the green colouring matter, the chlorophyll, present in the green parts of the plant. The relation of these substances to one another is, however, very complicated. For example, if we take an extract of chlorophyll and expose it to light the dye is bleached, but no permanent assimilation process goes on. The chlorophyll does not act as a catalyst, for if this were the case it could only hasten a reaction which would proceed slowly of itself, *i.e.* with a decrease in the free energy. The opposite course, as a matter of fact, is followed, the "natural" chemical forces being opposed and overcome, the free energy thereby increasing. The chlorophyll must therefore be used up in this process, the loss being made good by the living plant. It is no longer considered likely that the starch is the first substance formed; there are good grounds for believing that formaldehyde is the first substance formed and that it polymerises to higher carbohydrates. Another view, with less experimental justification however, is that the first product consists of formic acid and hydrogen peroxide; whilst a third view assumes the primary formation of oxalic acid from which formaldehyde and formic acid could be produced. It will be seen that no definite conclusions have as yet been reached.

The temperature coefficient of photochemical reactions is in general very small, but the carbon dioxide assimilation does not follow this rule. Thus between 0° and 10° the coefficient is 2·4; between 10° and 20° it is 2·1; and between 20° and 30° it is 1·8.

As regards the question of the velocity of assimilation and the colour of the light[1] employed, Draper showed many years ago that a maximum velocity was obtained with the yellow-green rays. This is in agreement with the general law that the rays which are absorbed are the chemically active ones. Draper's observation holds only for thick layers in which the absorption is nearly complete. For thin layers other parts of the spectrum play an important part. In connection with this it is of importance to note the observations of Engelmann (*Bot. Zeitung.*, 1883-84), who found that not only were the green cells of the plant capable of the assimilation, but likewise the brown and even red cells, and that the extent of the assimilation followed the same course as the optical absorption. Experimental results bearing upon this were obtained by Luther and Forbes in the quinine-chromic acid reaction. Since the ultra-violet waves were completely absorbed, even in very thin layers, while the violet were only slightly absorbed, by increasing the thickness of the layer, the amount of ultra-violet absorption would remain unchanged, but that of the violet increased. The spectral region of maxi-

[1] For a discussion of "Light Filters" *cf.* Plotnikow (*Zeitsch. physik. Chem.*, 79, 369, 1912); also C. Winther (*Zeitsch. Elektrochemie*, 9, 389, 1913).

mum efficiency depends therefore on the thickness of the layer, and this maximum does not necessarily correspond with the region of maximum absorption (the ultra-violet). In the green plant cells there is an optical absorption maximum in the red and in the blue, and a minimum in the green, whilst the yellow-green (for ordinary thicknesses) corresponds to the maximum assimilation efficiency.[1]

Attempts have been made to determine the *efficiency of photochemical reactions* quantitatively. By the efficiency is meant the ratio of the radiant energy turned into chemical work to the total energy absorbed by the system. In the case of the carbon dioxide assimilation this problem has been very thoroughly investigated by H. T. Brown and F. Escombe, *Phil. Trans.*, **193** B, 223, 1900; *Proc. Roy. Soc.*, **76** B, 29, 1905. Brown measured the quantity of carbon dioxide taken up by a leaf in a given time, and supposing it turned into a hexose, the energy transformed is simply the heat of combustion (with the sign changed) of the hexose (namely, 3760 cal.-grm.); 1 c.c. of carbon dioxide corresponded therefore to 5·02 calories of transformed light energy. It was observed at the same time that the assimilative power of the light was practically independent of the intensity of the light, this rather surprising result being probably due to the fact that under ordinary conditions the rays which were effective were in large excess,[2] the greater quantity passing through *without* absorption (and therefore not entering into the efficiency term as defined above). Brown further observed with a given leaf that the heat equivalent of the total light absorbed corresponded to 0·041 calories per cm.^{2} per minute, and that this corresponded in turn to the assimilation of 0·00034 c.c. of carbon dioxide per cm.^{2} per minute. Now the actual energy transformed into chemical work during the assimilation of 0·00034 c.c. of CO_2 is 0·00034 × 5·02 cals., or 0·0017 cals. per cm.^{2} per minute, and hence the ratio of $\frac{0{\cdot}0017}{0{\cdot}041}$ or 4·1 per cent. is the *percentage of the light transformed, in other words, the efficiency*. When, however, all allowance is made for the reflection of the light at the surface of the leaf and likewise the light which is simply transformed into heat without doing any chemical work, it is found that 98 per cent., or practically all the light energy actually absorbed by the *chlorophyll*, is converted into chemical work. For details of such calculation the original papers must be consulted. This large "efficiency" is, however, not met with in any other photochemical reaction so far investigated, and is probably connected in some way with the fact that the plant cell is "living". For the discussion of the anthracene-dianthracene case, *cf.* Weigert, *Ahrens Sammlung*, *l.c.*, p. 110, *seq.*

The term efficiency naturally calls to mind the Second Law of Thermodynamics, according to which (for any *reversible* process) the

[1] Reference should be made to the recent work of B. Moore, *Proc. Roy. Soc.*, 1914, who has shown that iron, especially in the colloidal form, is of great significance for assimilation.

[2] A criticism of Brown's work has been given by Tswett, *Zeitsch. physik. Chem.*, 76, 413, 1911, where the mechanism of the assimilation process is further discussed.

efficiency is given by $\frac{T_0 - T}{T_0}$, where T_0 is the temperature of the source of light and T the temperature of the reacting system. In all ordinary cases T is small compared to T_0, so that the thermodynamic efficiency is practically unity. The efficiency of a photochemical reaction is, however, evidently not determined by temperature alone.

We may conclude this brief account of the carbon dioxide assimilation process by describing Baur's carbon dioxide assimilation model. To appreciate this, however, it is necessary to say something first about photo-voltaic cells in general.

Photo-voltaic Cells.

(*Cf.* E. Baur, *Zeitsch. physik. Chem.*, **63**, 683, 1908; N. Titlestad, *Zeitsch. physik. Chem.*, **72**, 257, 1910; E. Baur, *Zeitsch. physik. Chem.*, **72**, 323, 1910; H. Schiller, *Zeitsch. physik. Chem.*, **80**, 641, 1912.)

When metals and other substances (solid salts) are exposed to ultra-violet light, it has been found that electrons in the free state are emitted from the surface. In some cases positively charged particles are also emitted. This phenomenon, which has been fairly thoroughly investigated, is known as the "photoelectric effect". This behaviour does not appear, however, to be identical with the phenomenon which we are about to discuss and known as the "photo-voltaic effect". In the latter we are dealing with the effect of light upon the electromotive force of a voltaic cell, that is with the effect of light upon electromotive behaviour of ions in aqueous solution. Although sufficient work has not yet been carried out to allow us definitely to say what the mechanism of the process is—it may be, for instance, an alteration, or tendency towards alteration, of the ordinary ionic equilibrium relations—yet the phenomenon is a marked one, and from its nature seems likely ultimately to throw a great deal of light upon the mechanism of photo-effects. It is necessary, therefore, that the student should make himself familiar with the phenomenon even at this stage. The sort of reaction which lends itself most readily to an investigation of this kind is that involving ionic oxidation or reduction. We shall restrict ourselves to a single case, namely, solutions of uranyl- and uranous salts. First of all let us consider the following system—

Platinum electrode	Solution of uranyl U^{+6} ions and urano U^{+4} ions	Saturated KCl	Calomel or hydrogen half element.

when *unexposed* to light. In a solution containing metallic uranium with uranous and uranyl salts, the equilibrium point lies over to the uranous side, *i.e.* considerable uranous concentration and small uranyl

concentration. Unless we happen to have chosen the equilibrium concentrations, a mixture of the two salts in the absence of the metal will exhibit an oxidation or reduction potential at the platinum electrode. It will be remembered that the platinum takes no part in the reaction; it simply serves as a means of transferring electrons to or from the solution, when the system is set up in the form of a cell such as that indicated above. If we make up the solution so that it contains an extremely large excess of uranous compared to uranyl ion, there will be a tendency to form uranyl at the expense of the uranous. That is, there will be a tendency for electrons to leave the uranous ions, and they can only do so by transfer to the electrode. We have the following reaction tending to take place—

$$U^{+4} - 2\ominus \rightarrow U^{+6}.$$

In such a case an oxidation process is tending to go on as regards the uranous-uranyl salt mixture. (Naturally if some foreign substance were added which could be reduced by the uranous ions, *reduction* of the *foreign* substance would take place in order that the uranous ions might be transformed into uranyl. This, however, would naturally not require an electrode, and would take place simply in a test tube, no electromotive force being obtained from it. The electromotive force which one obtains, however, in the case under consideration is a measure of the chemical effect of the uranous-uranyl salt mixture upon an oxidisable or reducible foreign substance.) To return to the case of the cell. If the reaction—

$$U^{+4} - 2\ominus \rightarrow U^{+6}$$

tends to occur or actually does occur even to a slight extent, there will be a transfer of electrons *from* the solution to the electrode. That is, current tends to flow from the electrode to the solution inside the cell. When the solution contains an excess of uranyl ions present, the U^{+6} ions now tend to transform themselves into U^{+4} ions; that is, a reduction of uranyl tends to go on at the electrode according to the equation—

$$U^{+6} + 2\ominus \rightarrow U^{+4}.$$

Current now tends to flow from the solution to the electrode. Titlestad's experiments show that over the entire range of uranous-uranyl mixtures examined by him the electrode was positive with respect to the normal hydrogen half element, that is, reduction of uranyl was tending to take place. The following numerical values are a few of those given by Titlestad, *l.c.*, and will illustrate the above processes:—

Millimoles of UO_2SO_4 per Liter.	Millimoles of $U(SO_4)_2$ per Liter.	Millimoles of H_2SO_4 also Present.	Potential of the Electrode against the Normal Hydrogen Electrode in volts.	Electrolytic Potential ϵ in Volts (Calculated) against the Hydrogen Electrode.
40	12	502	+ 0·353	0·402
27	24	502	+ 0·341	0·404
16	36	504	+ 0·321	0·402

The mean value of ϵ obtained from an extended series is—

$$\epsilon = 0{\cdot}404 \pm 0{\cdot}012 \text{ volts (against } H_2 \text{ electrode at } 25^\circ \text{ C.).}$$

It may be pointed out that we have treated the uranyl ion UO_2^{++} as though identical with U^{+6}. This is justifiable—as far as electromotive force values are concerned—since there is always an equilibrium existing between the two owing to hydrolytic decomposition, *viz.*—

$$UO_2^{++} + 4H^{\cdot} \rightleftarrows U^{+6} + 2H_2O.$$

Since, however, the UO_2^{++} is always present to a much greater extent than U^{+6}, it is usual to write the reactions with respect to uranyl. Thus the oxidation or reduction reaction which tends to take place at the platinum *may* be represented by—

$$U^{+6} + 2\ominus = U^{+4}$$

and when one takes into account the total reaction in the cell, using the hydrogen electrode as the other half element, the reaction equation is—

$$UO_2^{++} + 4H^{\cdot} + 2\ominus = U^{+4} + 2H_2O.$$

Employing the usual Peters' formula, we obtain for the observed electromotive force of the cell the expressions—

$$\pi = \epsilon + \frac{RT}{2F} \log \frac{[UO_2^{++}][H^{\cdot}]^4}{[U^{+4}]}$$

$$= \epsilon + 0{\cdot}028 \log \frac{[UO_2^{++}][H^{\cdot}]^4}{[U^{+4}]}$$

from which ϵ is calculated.

Experiment has shown that the above is a truly reversible oxidation-reduction process.[1] Now we turn to the question of the behaviour of such a system under the action of light. Titlestad, *l.c.*, employing ordinary platinum foil electrodes, set up a cell consisting simply of—

Platinum	Urano-uranyl	Urano-uranyl	Platinum

one-half of which was exposed to the light of a Nernst three-filament lamp, the other half being kept in the dark. *Under these conditions the cell showed quite a marked and steady electromotive force when unplatinised platinum was used.* Such a combination is a photo-voltaic cell. (Such a cell in the dark naturally gives rise to no electromotive force at all, since the two halves are identical.) The following table will illustrate the magnitude of the effects referred to:—

[1] Naturally whether a reduction or oxidation takes place in the cell depends to a large extent upon the other half element used, since the nett direction of current depends on the P.D.'s of both electrodes. In some of Titlestad's experiments, using the $\frac{N}{10}$ calomel electrode, oxidation instead of reduction actually took place.

Temperature, 25° C. Light Intensity = 2 (Titlestad's Scale)				
Percentage Composition. $\frac{25U^{+4}}{75U^{+6}}$		Percentage Composition. $\frac{75U^{+4}}{25U^{+6}}$		Conditions of Observation.
Time in Minutes.	E.M.F. in Millivolts.	Time in Minutes.	E.M.F. in Millivolts.	
0	0	0	− 1·6	Light off
2	− 25·4	2	− 27·7	Light on
4	− 42·6	4	− 40·4	,,
12	− 67·9	12	− 57·5	,,
16	− 71·3	16	− 58	,,
24	− 72·6	28	− 58	,,
2	− 65	2·5	− 48	Light off
20	− 41·1	20·5	− 23	,,
40	− 30·1	40·5	− 14·5	,,
50	− 26·4	60	− 10	,,

The light causes the exposed electrode to become *negative* compared to the other, *i.e.* current tends to flow inside the cell from the exposed to the unexposed electrode.

With constant light intensity the final or *maximum* values reached when exposure has been continued for a long time are dependent upon the composition of the mixture. The greater the amount of uranous salt present compared to uranyl, the smaller are the values of the electromotive force. That is to say, the more *uranyl* present, the more *negative* is the exposed electrode. Titlestad confirmed Baur's observation, *viz.* that there is a logarithmic relation between the intensity of the light and the maximal photo-electromotive force. Since the maximal photo-electromotive force is a function of the *total* concentration of uranium salt as well as of the sulphuric acid content, it is clear that the photochemical potential cannot be treated as a function of temperature and light intensity only. In other words, the photochemical potential of the urano-uranyl sulphate electrode does not obey the law of osmotic work. The equation which holds for the system in *the dark, viz.*—

$$\pi = \epsilon + 0{\cdot}028 \log \frac{[UO_2^{++}][H^+]^4}{[U^{+4}]}$$

cannot therefore be applied to the electrode exposed to light by simply adding a factor dependent upon the light intensity alone. This shows that the "light intake" (*Lichtsaugung*) is *not* a constant for a given substance, but depends on its concentration and possibly upon the presence of other substances. The existence of the phenomenon of "*Positivierung*," that is, the fact that the electromotive force after exposure has ceased, not only returns to zero in some cases, but actually crosses the zero point and sets up a potential difference in the opposite direction (the electrode now being positive), shows further how complicated this phenomenon is.

Some measurements have been made upon pure urano sulphate solution, and the careful determinations made by Schiller have shown a slight positive effect followed by a large negative one.[1] That is, on exposure the electrode becomes first positive and then reverses, becoming markedly negative even as high as 0·3 volt. We must assume, therefore, that both uranous and uranyl ions are photosensitive (as Schiller's experiments with solutions of the pure salts have shown), and further that the uranous is much more sensitive than the uranyl. With a solution of pure uranous salt exposed to light in the cell, the exposed electrode (ultimately) becomes *negative*. This naturally fits in with the supposition that the light tends to increase the oxidising tendency (*i.e.* the transfer of electrons *to* the exposed electrode). What the mechanism of the process is we do not know. Baur simply considers that the light alters the thermodynamic potential of the ions to different extents. This is no doubt true, but is too general to be regarded as an explana tion. Baur further considers as possible the following reactions at the exposed region—

$$2U^6 \rightleftarrows U^4 + U^8$$
$$3U^4 \rightleftarrows 2U^3 + U^6$$
$$U^4 + U^6 \rightleftarrows 2U^5.$$

The substances on the right-hand side being unstable, those on the left must have their chemical potential raised by the light in order to produce them. For further information upon this interesting subject the papers quoted should be referred to.

E. Baur's Carbon Dioxide Assimilation Model.

The problem of the assimilation of carbon dioxide from the standpoint of reversible thermodynamic process has been approached in a very ingenious manner by Baur (*Zeitsch. physik. Chem.*, **63**, 683, 1908), and although this is by no means the final solution of the question, it is of importance in at least pointing the way. In the actual case carbon dioxide is by some means reduced through the action of sunlight and the chlorophyll, the ultimate products being complex organic compounds. With such an arrangement as this, about which we know practically nothing, it would be hopeless to attempt to visualise any reasonable reversible mechanism of the processes involved. Baur has therefore confined his attention to a more simple process of an *analogous* nature. The first question which arises is, What is the first step in the process? Baur assumes that the carbon dioxide is first converted into oxalic acid. We shall accept this provisionally as correct. This in turn probably produces formic acid, and this in turn formaldehyde, which may polymerise into the carbohydrates and oxyacids which we know to be formed as final products in the plant. Let us confine our attention to the first step only, namely, the conversion of carbon dioxide into oxalic acid.

[1] This occurs not only in the case of pure uranous salt, but also when some uranyl (up to 10 per cent.) is likewise present.

The simplest way of looking at this is to regard it as an *electrolytic* process taking place at an electrode of pure platinum, the electrode being necessary as a transfer of electrons has to take place in order to allow the process—

$$2CO_2 \rightarrow C_2O_4^{--} + 2 \oplus$$

to take place. This is the fundamental equation of the step as written by Baur. Since, however, we do not as yet recognise the physical existence of positive electrons, the following modification of the equation would appear to correspond more closely to an actual process, *viz.*—

$$2CO_2 + 2 \ominus \rightarrow C_2O_4^{--}.$$

That is, two uncharged molecules are supposed to receive two electrons (from the electrode), thereby forming the anion of oxalic acid. If we set up a cell, one half being the calomel or hydrogen electrode, the other half element being a piece of platinum dipping into an aqueous solution of carbon dioxide, and neutral electrolyte, we should expect a certain electromotive force corresponding to the process indicated above, and we should expect some of the carbon dioxide to disappear, and oxalanion to be produced in the solution. Such a process, however, even in powerful light, does not apparently take place rapidly enough to allow of potential measurement. If it goes on at all it is only infinitely slowly. What we have to do, therefore, is to try and catalyse it by making use of a rapid ionic reaction of the oxidation-reduction type, and at the same time make the light an essential part of the process which, as a whole, must be reversible. A possible way of carrying this out is effected by Baur's model, the catalysts employed being ferrous and ferric salts[1] and silver chloride.

The model is shown diagrammatically in the figure (Fig. 55). A vessel is divided into three chambers, *a*, *b*, *c*, by a photochloride slab and a semi-permeable membrane. The entire vessel is filled with a dilute solution of hydrochloric acid. The photochloride is a homogeneous solid solution consisting of silver chloride and amorphous silver (*cf.* K. Sichling, *Zeitsch. physik. Chem.*, **77**, 1911 ; also Reinders, *Zeitsch. physik. Chem.*, **72**, 356, 1911). It is sensitive to light, and under its influence the silver chloride could react with the water in (*a*) according to the equation—

$$2AgCl + H_2O \rightarrow 2Ag + 2HCl + \tfrac{1}{2}O_2.$$

This has been experimentally verified.

When this happens the concentration of silver in the photochloride

[1] The use of iron salts is naturally suggested by Schafer's observation (*Zeitsch. physik. Chem.*, **72**, 308, 1910) that a solution of ferrous oxalate and potassium oxalate in the presence of carbon dioxide at 50° C., and at 1 atmosphere pressure, slowly absorbs a small amount of carbon dioxide, ferric oxalate being formed. Also measurements of the oxidation-reduction potential of ferrous and ferric oxalate ions have shown that reproducible values are obtained, and that using different concentrations of *ous* and *ic* salt, one can calculate in the ordinary way the electrolytic potential ϵ, which is found to be 0·02 volts with respect to the hydrogen electrode. All these effects refer to reactions in the dark. In the light Baur has found that ferric oxalate solution gives off carbon dioxide.

rises. We shall see the significance of this in a moment. In compartment *c* we have some ferrous oxalate and ferric oxalate ions (from the corresponding potassium salt). As already stated, these are in equilibrium, the reaction between them being—

$$K_3Fe(C_2O_4)_3 \rightarrow K_2Fe(C_2O_4)_2 + \tfrac{1}{2}K_2C_2O_4 + CO_2.$$

This reaction is a reversible one. Stating the above reaction in terms of ions and using the symbol $\rightleftarrows$ to indicate that equilibrium is established, we may write—

$$Fe(C_2O_4)_3''' \rightleftarrows Fe(C_2O_4)_2'' + \tfrac{1}{2}C_2O_4'' + CO_2 \quad . \quad . \quad (1)$$

Above the compartment (*c*) there is a space containing carbon dioxide, and the pressure of the carbon dioxide is one of the determining factors of the ionic equilibrium referred to in equation (1).

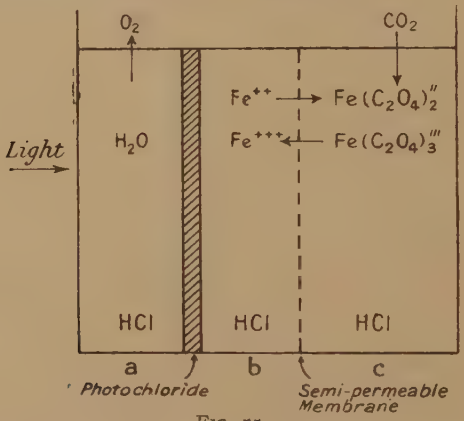


FIG. 55.

The ferric and ferrous complex ions which take part in (1) will also further decompose according to the equations—

$$Fe(C_2O_4)_3''' \rightleftarrows Fe^{+++} + 3(C_2O_4)'' \quad . \quad . \quad . \quad (2)$$

and

$$Fe(C_2O_4)_2'' \rightleftarrows Fe^{++} + 2(C_2O_4)'' \quad . \quad . \quad . \quad (3)$$

The semi-permeable membrane is supposed to be permeable to the ions Fe^{+++} and Fe^{++} and also to hydrochloric acid. It is impermeable to the complex ions $Fe(C_2O_4)_3'''$ and $Fe(C_2O_4)_2''$. In chamber (*b*) we shall therefore have ferrous and ferric ions, these being in equilibrium with those in chamber (*c*) since the membrane is quite permeable to these. The potential of the ferri-ferro equilibrium is so arranged that it is identical with that of the photochloride against the hydrochloric acid or Cl′ in (*b*).

As long as (*a*) is unexposed to light the whole arrangement is in equilibrium. Now suppose light passes into (*a*), as indicated in the diagram. The following reaction, as we have already seen, occurs in (*a*)—

$$\text{Light} + 2AgCl + H_2O \quad 2Ag + 2HCl + \tfrac{1}{2}O_2 \quad . \quad (4)$$

The silver produced by this means diffuses evenly through the photochloride, and part of it appears at the other side of the slab. Now at this (*b*) side there was a potential between the photochloride and the Cl′ and the ferrous-ferric solution, the equilibrium having been altered owing to the altered composition of the solid photochloride. As this now contains too much silver, we should have the following reaction occurring—

$$Ag + Cl' \text{ (from the HCl)} + Fe^{+++} \rightarrow AgCl + Fe^{++} \quad . \quad (5)$$

Some ferrous ion has now been produced in (*b*) at the expense of the ferric. Diffusion of these ions in opposite directions occurs across the membrane, some ferric passing into (*b*) and some ferrous passing into (*c*). The ferro-ferri ion equilibrium in (*c*) is thus upset, there being now too much Fe^{++}, and in order to reach the equilibrium again some of the ferrous has to disappear and give rise to ferric according to the equation—

$$Fe^{++} + 2CO_2 \rightarrow C_2O_4'' + Fe^{+++} \quad . \quad . \quad (6)$$

In this last process some of the carbon dioxide has been used up to form C_2O_4'', which is the desired reaction, and this may now take place rapidly since it is part of the naturally rapid ionic adjustment characteristic of ferrous-ferric mixtures. The nett result of equations (1) to (6), as will be found by adding them together, is—

$$2CO_2 + H_2O + \text{light} \rightarrow H_2C_2O_4 + \tfrac{1}{2}O_2.$$

The photochloride and the iron salts act only as intermediaries.

The fact that each step of the process is of a reversible kind allows one to conclude that if the oxygen and oxalic acid which have been produced as above under the action of light be now set up in the form of a cell containing electrodes, reversible with respect to oxygen and oxalic acid respectively, we should receive an electromotive force from the cell (in the dark), current being produced; the electric energy thus obtained being equivalent to the light energy photochemically utilised in the earlier process. Such a cell would be a photochemical accumulator.

Baur discusses the problem at greater length, but sufficient has been said to indicate the principal idea.

Note.—It has not been possible to find room for the photo-phenomenon called Solarisation. A very full discussion of the problem is, however, easily available to English readers in the papers of W. D. Bancroft, *Jour. Phys. Chem.*, 1909-1910.

Thermodynamics of Reversible Photo-Reactions Involving a Gain in Free Energy at the Expense of the Light.

Byk's Theory.

This theory was put forward by Byk (*Zeitsch. Elektrochemie*, **14**, 460, 1908; *Zeitsch. physik. Chem.*, **62**, 454, 1908). It consists in the first instance of thermodynamical considerations, which of course, if

properly applied, should hold good whatever the actual mechanism of the process is, as long as it is reversible. As regards the mechanism of the photochemical action, Byk considers that it may be regarded as essentially a rapidly alternating electrolytic process. In this connection the significance of the work of Grotthus has been brought out in the very comprehensive articles by W. D. Bancroft, *Jour. Phys. Chem.*, **12**, 1908, on the "Electrochemistry of Light". This can at least be regarded as plausible when one remembers that light itself is an electromagnetic phenomenon. Byk starts with the assumption that "no transformation of *material*, but only of *energy*, is caused by the intensity of the incident light, *i.e.* the light energy, and that the work performed against chemical forces is proportional to the light energy". We shall now follow out Byk's thermodynamical reasoning, taking as an instance of a reversible reaction in which work is gained the reaction—

$$\text{Anthracene} \rightleftarrows \text{dianthracene in solution}$$

which has been investigated by Luther and Weigert. In the *dark* the natural reaction, *i.e.* reaction involving decrease of free energy, is the depolymerisation process, *viz.* dianthracene → 2 anthracene. In the presence of light the reverse reaction, 2 anthracene → dianthracene, takes place.

Let V be the total volume of the solution, [D] and [A] the concentration in gram-moles per c.c. of dianthracene and anthracene present in the solution, ϵ the work done in transforming isothermally and reversibly 1 mole of dianthracene into 2 moles of anthracene, supposing each to be present at unit concentration (1 mole per c.c.), which, of course, does not represent the equilibrium state. An equal and opposite amount of work would be done in the polymerisation process. (*Note that this work-term, being a thermodynamic work-term, does not mean that the process is, in the actual case, necessarily brought about by light. No matter how the change is brought about, as long as it is done reversibly, the osmotic work under the conditions as regards concentration mentioned will be* ϵ.) Let T be the absolute temperature, and R the gas constant. The solution is considered sufficiently dilute for the simple gas laws to apply. Let k be the velocity-constant in the dark (depolymerisation of dianthracene), t the time, E_A the total energy absorbed in unit time by the anthracene present in the solution, α the efficiency factor or fraction of unit light energy absorbed, which is turned into chemical work. Luther and Weigert carried out measurements of the absorption of the anthracene and dianthracene in phenetol solution, as well as that of the solvent itself. The extinction coefficient is given by the expression—

$$m = \frac{1}{cl} \log \frac{I_0}{I}.$$

Where c represents concentration of the substance in millimoles per liter, l the thickness of the layer traversed by the light, I_0 the initial intensity of the light, and I the intensity after traversing the layer l. Measurements by Luther and Weigert gave the following approximate results—

For phenetol $m_{(1\text{ cm.})} = 0{\cdot}21$
dianthracene $m_{(1\text{ cm.})\ 1\text{ millimole per liter}} = 0{\cdot}21$
anthracene $m_{(1\text{ cm.})\ 1\text{ millimole per liter}} = 0{\cdot}56$

This calculation is made on the assumption, which can only be an approximate one, that the extinction-coefficient of a given substance is independent of the other substances present. It will be noted that anthracene possesses a much greater absorption than dianthracene. In the theoretical treatment of the subject given by Byk we take into consideration only the light absorbed by the anthracene. The *sensitivity* of anthracene to light (as shown by its polymerising) is enormously greater than that of dianthracene; that is the efficiency factor α for anthracene is very great compared to that for dianthracene or phenetol. When the total light energy absorbed by the anthracene is E_A, the part converted into photochemical work is αE_A, the remainder being converted into heat and then dissipated.

The term ϵ.—Let us think of two very large boxes, one with dianthracene at concentration [D], and the other with anthracene at concentration [A], these two terms not representing equilibrium concentration. The question is, what is the work done by the system, *i.e.* by the chemical forces in transforming 1 mole of D into 2 moles of A? Suppose A_0 and D_0 represent the equilibrium concentration values of the two substances in the *dark*. Consider a large box with these substances present.

First Step.—Take 1 mole of D from concentration [D] to equilibrium concentration $[D_0]$.

$$\text{Work} = -\int_1^2 vdp = \int_2^1 vdp = \text{RT log } \frac{[D]}{[D_0]}.$$

Now let the molecule of D [at D_0] change without work into 2 molecules of A [at A_0] (the principle of the equilibrium box).

Second Step.—Then remove these 2 molecules of A from $[A_0]$ to [A].

$$\text{Work} = 2\text{RT log } \frac{[A_0]}{[A]}.$$

Hence the total work of transformation (1) and (2)

$$= \text{RT log } \frac{[D]}{[D_0]} + \text{RT log } \frac{[A_0]^2}{[A]^2} = \text{RT log } \frac{[D]}{[A]^2} + \text{RT log } \frac{[A_0]^2}{[D_0]}.$$

We can write $\text{RT log } \frac{[A_0]^2}{[D_0]} = -\text{RT log } \frac{[D_0]}{[A_0]^2}$, which is $-\text{RT log } K_0$, where K_0 is the equilibrium constant $\frac{[D_0]}{[A_0]^2}$, for the dark equilibrium point. ϵ has been defined as the work done in transforming 1 mole of D, at unit concentration, [1], into 2 moles of A, also at unit concentration. That is—

$$\epsilon = \text{RT log } \frac{[1]}{[D_0]} + \text{RT log } \frac{[A_0]^2}{[1]^2}$$

$$= \text{RT log } \frac{[A_0]^2}{[D_0]} = -\text{RT log } K_0.$$

Hence the work done by the system in transforming isothermally and reversibly 1 mole of D at concentration [D] into 2 moles of A at [A], or *vice versâ*, is numerically—

$$\epsilon + RT \log \frac{[D]}{[A]^2}$$

(simply the van 't Hoff isotherm).

When the transformation takes place in the direction of depolymerisation $D \rightarrow 2A$ this is the natural way along which the chemical forces act. Again, consider the solution having arbitrary concentration terms [D] and [A], which are not equilibrium values, and expose it to light. Either anthracene or dianthracene will be formed, depending on the initial quantities of D and A respectively. Suppose we start with a solution containing a large quantity of A and a small quantity of D, D will be formed, and the work done by the light absorbed will be, first, that of retransforming the amount of A which would have been formed from D, during the time considered, by the ordinary "dark" reaction which tends to take place whether the light is present or not. Secondly, there is the work required for the formation of a fresh quantity of D which actually takes place. (Note.—If the relative values of [D] and [A] are initially such that we have overstepped the "light equilibrium" point, *i.e.* there is too much D, the light energy absorbed is not sufficient to compensate the "dark" reaction, and only serves to slow it down. We are considering, however, for the sake of simplicity, the case in which D is actually formed.) As already seen, the work done by the light (in sense opposite but equal to the natural chemical work) in the actual production of 1 mole of D under the given concentration condition is—

$$\epsilon + RT \log \frac{[D]}{[A]^2}.$$

If dD is the newly-formed quantity of D in gram-moles per c.c. in the time dt, the work done in the solution in time dt due to the *formation* of D is—

$$VdD\left(\epsilon + RT \log \frac{[D]}{[A]^2}\right).$$

In order to nullify the natural chemical decomposition of D which takes place in the dark and happens to be a monomolecular one, $C_{28}H_{20} \rightarrow 2C_{14}H_{10}$, the energy required is—

$$Vk[D]dt\left(\epsilon + RT \log \frac{[D]}{[A]^2}\right).^1$$

The sum of both reactions represents the total work done by the

[1] The velocity-constant must come into this term when the physical meaning of k is borne in mind, namely, the rate at which a body is decomposing per unit of time, or in fact the amount of the body changed in unit time if the concentration of the body were kept at unity throughout. $V[D]kdt$, therefore, is the mass of D which *would be* transformed in time dt in the dark, the concentration being [D] per c.c., and the total volume being V c.c.

light during time dt. The quantity of light which has actually accomplished this is $a\mathrm{E}_A dt$. We obtain, therefore—

$$a\mathrm{E}_A dt = \mathrm{V}d\mathrm{D}\left(\epsilon + \mathrm{RT}\log\frac{[\mathrm{D}]}{[\mathrm{A}]^2}\right) + \mathrm{V}k[\mathrm{D}]dt\left(\epsilon + \mathrm{RT}\log\frac{[\mathrm{D}]}{[\mathrm{A}]^2}\right)$$

or

$$\frac{d\mathrm{D}}{dt} = \frac{a\mathrm{E}_A}{\mathrm{V}\left(\epsilon + \mathrm{RT}\log\frac{[\mathrm{D}]}{[\mathrm{A}]^2}\right)} - k[\mathrm{D}] \quad . \quad . \quad (1)$$

This gives the rate of formation of D under the influence of light. Byk points out that the same expression, with sign changed, is obtained in the case above mentioned where, even under the influence of light, the D decreased (if the system has been arbitrarily chosen so that it initially has too much D). In the stationary state (*i.e.* the photochemical "equilibrium" point), under a given constant light energy at a given temperature, the rate of formation of D is just balanced by the rate of decomposition, *i.e.* $\frac{d\mathrm{D}}{dt} = 0$, and hence at this point—

$$k[\mathrm{D}]\mathrm{V}\left(\epsilon + \mathrm{RT}\log\frac{[\mathrm{D}]}{[\mathrm{A}]^2}\right) = a\mathrm{E} \quad . \quad . \quad . \quad (2)$$

If we denote by $[\mathrm{D}_l]$ the concentration of D which is in photochemical stationary state with [A] under a light energy absorption $a\mathrm{E}_A$, we can write the above equation—

$$\frac{a\mathrm{E}_A}{\mathrm{V}} = k[\mathrm{D}]\left(\epsilon + \mathrm{RT}\log\frac{[\mathrm{D}_l]}{[\mathrm{A}]^2}\right)$$

and hence equation (1) may be transformed into—

$$\frac{d\mathrm{D}}{dt} = k[\mathrm{D}_l]\left(\frac{\epsilon + \mathrm{RT}\log\frac{[\mathrm{D}_l]}{[\mathrm{A}^2]}}{\epsilon + \mathrm{RT}\log\frac{[\mathrm{D}]}{[\mathrm{A}]^2}}\right) - k[\mathrm{D}] \quad . \quad . \quad (3)$$

The value of ϵ may be obtained from equation (2) by carrying out two experiments in which stationary states are reached, the absolute values of A and D differing in each case. E_A has then different values, *viz.* E_A' and E_A'', corresponding to the different [A] values. The same absolute amount of light energy E, to which the solution is exposed, is used in both cases, and Luther and Weigert have given a formula [1] which is found to hold good between E and E_A corresponding to differing values of [A]. In this way Byk calculated ϵ to be $72{\cdot}68 \times 10^{10}$ erg,

[1] The formula is—

$$\mathrm{E}_A = \frac{m_A \cdot [\mathrm{A}] \cdot 10^6}{m_A \cdot [\mathrm{A}] \cdot 10^6 + m_D \cdot [\mathrm{D}] \cdot 10^6 + m_{\text{phenetol}}} \cdot \mathrm{E}$$

where m_A, m_D and m_{phenetol} are the extinction coefficients of anthracene, dianthracene, and the solvent phenetol respectively, which can be experimentally determined. The factor 10^6 comes in Byk's paper owing to using gram-mole per c.c. as concentration instead of millimole per litre as employed by Luther and Weigert (*cf.* Byk, *Zeitsch. physik. Chem., loc. cit.*, p. 460).

or 17,206 gram-calories. ϵ represents the work done in the transformation of 1 mole of D $\rightarrow$ 2 moles of A. The work done at constant volume will be $\epsilon - RT \log 2$, since $RT \log 2$ is the osmotic work which has to be done to compress the system to the volume occupied by the original material. The work done at constant volume is therefore 16,610 gram-calories. A further control of the value of ϵ may be obtained by using it to calculate the equilibrium value of A and D in the dark at equilibrium point, for we have already seen that—

$$\epsilon = RT \log \frac{[A_0]^2}{[D_0]}.$$

Luther and Weigert carried out an experiment in which 0·4785 gram of D was dissolved in 40 grams of phenetol. After 30 hours' boiling in the dark at 170° C. no detectable quantity of D was present. The value of the concentration of A (produced from the D), which is therefore A_0, is $5{\cdot}507 \times 10^{-5}$ gram-mole per c.c. If we were to apply the above expression, using the known values for ϵ and A_0, we should find that $D_0 = 7{\cdot}175 \times 10^{-18}$ gram-mole per c.c., which, of course, would be quite undetectable, as experiment shows.

Hence $K_{0_{170^\circ\,C.}}$ is $= 1{\cdot}303 \times 10^{-13}$.

By means of equation (2) and the value of ϵ we can calculate αE_A.

If now with constant light quantity E absorbed (by solution as a whole) and constant volume, the relation of the stationary state concentration of D and of A is investigated, then, as was first observed by Luther and Weigert, we find the remarkable fact that even when enough substance is present to make the absorption of light *complete*, the observed values of the D_l concentrations at first rises (in different experiments containing increasing absolute quantity of A), but becomes nearly constant when the concentration of the A is above 200 millimoles per liter.[1] Luther and Weigert could only explain this phenomenon upon the assumption of the presence of a strongly thermal absorbent inter-

[1] In the stationary state produced by light we have a state of things differing in *principle* from the equilibrium point reached in the dark owing to ordinary chemical attractions acting according to the Law of Mass Action. Thus in the dark the system would so change that the value of $\frac{[D_0]}{[A_0]^2}$ would be *constant* whatever the absolute value of A or of D were. In the stationary state, however, such is not the case. Even with the same incident light energy and temperature, the value of $\frac{D_l}{[A]^2}$ is not at all constant, but varies with the absolute amounts of the constituents present. The thermodynamical theory given is, however, in agreement with this, *i.e.* it does not assume that there should be a mass action equilibrium at the stationary state. Thus at first sight one would think that the work done in taking 1 mole from the dark equilibrium point (constant $= K_0$) to the light equilibrium point ("K_l" = "constant") would be simply $RT \log \frac{K_0}{K_l}$. This, however, has no meaning, for K_l has no real significance as a constant. According to Luther, a *real* photochemical equilibrium analogous to the dark equilibrium could only arise if the system at the same time had the same temperature as the surrounding "light jacket".

mediate compound. The present thermodynamical considerations alone are sufficient to predict this behaviour. Thus let us write equation (2), substituting the whole energy absorption E instead of E_A, which is nearly true. Then—

$$k[D]V\left(\epsilon + RT \log \frac{[D]}{[A]^2}\right) = \alpha E \cdot \frac{m_A[A]10^6}{m_A[A]10^6 + m_D[D]10^6 + m_{\text{phenetol}}} \quad . \quad (4)$$

(For large values of A the factor multiplied on αE becomes nearly unity.) Employing the above equation, Byk has calculated the values of $[D_l]$, which for a given E ought to be in "light equilibrium" with given values of [A]. The following table shows the extent of the agreement found :—

[A]	10	20	40	80	120	160	240	300	400	millimoles per liter.
Calculated [D]	6·24	7·15	7·95	8·64	**9·01**	9·27	**9·62**	9·82	10·07	
Observed [D]	3·72	4·59	5·71	7·80	9·01	9·09	9·62	9·57	—	

(The values in heavy type were employed for the calculation of the constants.) The figure (Fig. 56) shows these results graphically, Curve 1

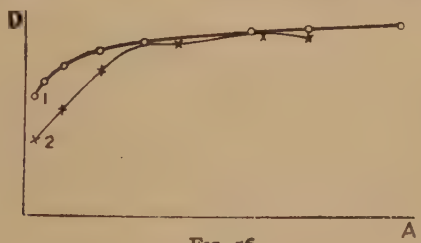


FIG. 56.

being the calculated, Curve 2 being the observed values of Luther and Weigert. It will be seen that at the higher range of A concentration the agreement between the observed and calculated [D] is good. *At small [A] values the difference is great, and greater the less A is present. This cannot be accounted for on pure thermodynamic grounds at the same time taking α to be constant, but, according to Byk, on electromagnetic grounds (in opposition to Luther and Weigert's view of heat-absorbing intermediate compounds).* An important point is the practical independence of the D concentration in relation to the A concentration for high values of the latter, required by the thermodynamic theory and actually obtained as the table shows.

The "light equilibrium" or stationary state concentration of D increases in general with increasing light energy, but there is always a lag. This is seen to be predicted by the theory from equation (4), which may be rewritten—

$$\frac{kV}{m_A \cdot [A] \cdot 10^6} \cdot [D] \cdot \left(\epsilon + RT \log \frac{[D]}{[A]^2}\right) (m_A \cdot [A] \cdot 10^6 + m_D \cdot [D] \cdot 10^6 + m_{\text{phenetol}}) = \alpha E \quad . \quad (5)$$

If now E be increased n-fold, then if D also increased n-fold, the expression on the left-hand side would be too large, *i.e.* the equation would not hold, for in this we have powers of D higher than 1. If, therefore, in two experiments the light energy ratio is $\frac{E_1}{E_2}$, then this is greater than the corresponding ratio $\frac{[D_1]}{[D_2]}$. In the following table are such values calculated by means of equation (5), and the observed values obtained from Luther and Weigert's data :—

[A] Millimole per Liter.	$\frac{E_1}{E_2}$.	$\frac{[D_1]}{[D_2]}$ Found.	$\frac{[D_1]}{[D_2]}$ Calculated.
40	1·52 : 1	1·43 : 1	1·46 : 1
40	0·4 : 1	3·7 : 1	3·6 : 1
40	0·9 : 1	7·8 : 1	7·7 : 1
10	0·9 : 1	7·6 : 1	7·3 : 1

The agreement is fairly good.

Stationary State and Temperature.

Luther and Weigert have shown that as temperature is *raised* the concentration of D falls in the stationary state, other conditions being maintained the same, *i.e.*—

$$\frac{D_{l_T} + 10}{D_{l_T}} = 0{\cdot}34 \text{ in one experiment.}$$

This must be carefully distinguished from the temperature effect upon K_0 or $\frac{[D_0]}{[A_0]^2}$, the dark true equilibrium point, where D rises with rise in temperature.

The Velocity of Photopolymerisation.

Considering equation (3), we see that the factor $\left(\frac{\epsilon + RT \log \frac{[D_l]}{[A]^2}}{\epsilon + RT \log \frac{[D]}{[A]^2}}\right)$ is very nearly unity, for ϵ is a large quantity (Byk gives other considerations supporting this conclusion: *cf. Zeitsch. Elektrochem.*, *l.c.*, p. 464). We can therefore write—

$$\frac{dD}{dt} = k[D_l] - k[D] \quad . \quad . \quad . \quad . \quad (6)$$

$k[D]$ is evidently the velocity of the true monomolecular dark reaction of depolymerisation. The term $k[D_l]$ should therefore approximately represent the initial velocity of polymerisation, *i.e.* at the stage when

the back reaction is negligible. We have seen that for small A concentrations theory and experiment do not agree very well in connection with photo-*equilibrium* points, so we shall pass on to the region of larger [A], where the theoretical and experimental curves already given lie close to one another. In this region (*cf.* Fig. 56, already given) the quantity of $[D_l]$ is almost independent of A, so that we can regard $[D_l]$ as a constant (b) and write—

$$\frac{dD}{dt} = kb - k[D] \quad . \quad . \quad . \quad . \quad (6A)$$

Writing K_l for kb, we obtain—

$$\frac{dD}{dt} = K_l - kD \quad . \quad . \quad . \quad . \quad (7)$$

which has the same form as the equation found experimentally by Luther and Weigert for the velocity of D formation in the region of higher A concentration. As regards the order of the polymerisation reaction, Luther and Weigert found that it lay between 0 and 1. Byk points out that this is to be expected from equation (3) (*i.e.* in equation (7), if the term kD were negligible the equation $\frac{dD}{dt} = K_l$ is evidently of zero order).

The temperature coefficient of the light action, *i.e.* polymerisation, has been found by Luther and Weigert to be very small. It increases with temperature rise (1·1 average increase per 10° C.). Byk shows that the magnitude of this effect is also to be expected, say from equation (6A). Experimentally, the value of $\frac{k_T + 10}{k_T}$, where k is, of course, the velocity constant in the dark = 2·8 (Luther and Weigert); also

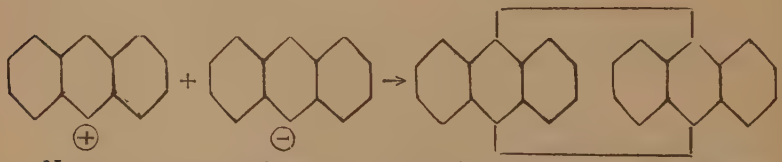
$$\frac{[D_l]_T + 10}{[D_l]} = 0{\cdot}34$$

(Luther and Weigert), and hence for the product of the two we obtain 0·95, while Luther and Weigert obtained 1·1.

Byk's Electromagnetic Theory.

So far we have considered Byk's thermodynamic theory, now we pass on to consider the electromagnetic considerations which he brought forward to complete the theoretical treatment of the reversible photo-reaction. First consider the discrepancies between the A and D stationary state values for the region of small A (*cf.* Fig. 56). The quantity of D_l actually found in this region is considerably less than the calculated. On the basis of foregoing considerations Byk points out that this means that, with decreasing amounts of A present, a larger and larger fraction of the light energy is *not* used for photochemical work, but for other purposes—in all probability for heat. That is, the efficiency factor a is not a constant, but depends on the actual amount of A present. (We should, of course, expect *à priori* the term aE_A to

decrease with A, but we have assumed hitherto that α itself is constant —which we can no longer consider to be the case.) To account for this, Byk employs the following train of reasoning: It is a well-established fact that the electrical resistance (of electrolytes) increases with decreasing concentration and temperature. Now with regard to continuous current, anthracene solutions are practically non-conductors. To rapidly *alternating* current, such as light, this would not be the behaviour, for the charged particles present in the molecules could resonate and take over from the ether (which "conducts" the light) a part of the oscillating current, *i.e.* they would become conductors for rapidly alternating current. Now, it is evidently possible from this standpoint that for sufficiently strong external electromagnetic forces (*i.e.* great intensity of light) the vibrating charged particles in a given molecule might possess such an amplitude that they would be *free*, and possibly come under the influence of a neighbouring molecule, which would thus lead to the possibility of a chemical union of the two neighbouring molecules, *i.e. photo-polymerisation.* Byk cites the cases of the ionising of gases and the photo-electric effects of solid surfaces (shown actually by anthracene itself), as well as the alteration of conductivity of selenium, sulphur, and silver chloride, as evidence for the loosening effect of light waves upon the electronic constituents of various sorts of molecules. According to Byk, therefore, we have the temporary formation of + and − ions (very similar to electrolytic ions), consisting of the molecules which have temporarily lost an electron and those which have gained one. The actual process of union (polymerisation) might, therefore, be represented thus—



Now we come to an important conclusion. The fewer A molecules there are present the greater will have to be the distance traversed by the charged particles, before one such charged particle can come under the attraction of another of opposite sign, in order to allow of the possibility of polymerisation. But the greater the distance throughout which the particles remain unneutralised the greater the acceleration which will be set up, and hence a larger quantity of the light energy absorbed (since it entails friction with the ether) will be converted into heat, and the quantity of light thus converted into heat will be the greater the further apart the A molecules are, *i.e.* the less the concentration of the A molecules. *Cf.* Byk, *Zeitsch. physik. Chem.*, *loc. cit.*, p. 482. That is, on electromagnetic grounds one would expect that with small A concentration the fraction of the light (of constant total E) which is available for *purely* chemical work is less than in the case where the A molecules are more crowded. That is, α should decrease with decreasing concentration of A, which fits in with the observed facts. This is,

of course, only qualitative agreement. Byk has, however, endeavoured to treat it more quantitatively. Thus the *temperature coefficient of the velocity* of the light reaction is of the same order as the temperature coefficient for the mobilities of the electrolytic ions. The value given was 1·1, which, however, only holds for a certain narrow range of anthracene concentration and temperature. Extreme values are 0·98 and 1·51, that is the increase in velocity of the light reaction varies from 0 to 50 per cent. Ionic mobilities also increase from 15-27 per cent. for a rise of 10° C. The order of magnitude is therefore the same as it should be on the electromagnetic view. α is therefore a function of temperature increasing with it on the magnetic view, since friction decreases as temperature rises.

Effect of Temperature on the Value of the D concentration in a Stationary State.

Consider equation (2)—

$$k[D_l]V\left(\epsilon + RT \log \frac{[D]_l}{[A]^2}\right) = \alpha E_A.$$

As temperature rises, α, as we have seen from the electromagnetic standpoint, also increases. On the left-hand side the value of T likewise rises, as also does the dark velocity constant k. We cannot therefore say whether the ratio of $\frac{[D]}{[A]^2}$, *i.e.* $\frac{[D_l]}{[A]^2}$, alters or not; it may increase or decrease.

Weigert has shown that D_l *diminishes* with *rise* in temperature. As already mentioned, this is to be clearly distinguished from the dark equilibrium state for which Weigert has shown experimentally that D is more stable the higher the temperature, *i.e.* he has shown that the dark equilibrium constant $\left(\frac{[D_0]}{[A_0]^2}\right)$ *increases* with temperature. This is the same as saying that since—

$$\epsilon = -RT \log \frac{[D_0]}{[A_0]^2} \text{ or } = +RT \log \frac{[A_0]^2}{[D_0]}$$

ϵ increases in virtue of the rise in T but decreases in virtue of the increase in D_0. Weigert shows that—

$$\frac{d \log K_0}{dT} = + \frac{4330}{T^2},$$

and therefore that—

$$\frac{d}{dT}(RT \log K_0) = R \log K_0 + RT \times \frac{4330}{T^2} = R \log K_0 + \frac{R}{T} 4330.$$

That is—

$$\frac{d\epsilon}{dT} = -R \log K_0 - \frac{R}{T} 4330.$$

Employing the data given by Weigert (*Ber. D. chem. Gesell.*, **42**, 852, 1909), log $K_0 = -1{\cdot}82$ at 85° C., and hence at this temperature—

$$\frac{d\epsilon}{dT} = +1{\cdot}985 \times 1{\cdot}82 - \frac{1{\cdot}985 \times 4330}{358} = -20 \text{ (approx.)}.$$

That is, ϵ decreases as temperature rises, at least at a temperature of 85° C. With much higher temperatures it could become positive. (This is not pointed out either by Byk or Weigert, but the temperature is probably outside the limits at which the solutions could exist as liquid.)

So far we have discussed the joule current heat (which, if the current were continuous would be C^2R) and likewise the energy used for photochemical work. Besides these two, there is probably a third kind of energy absorption which is probably of greater magnitude, namely, the purely thermal absorption of the system. This is due to the energy consumed in the friction of the quasi-elastic vibrating bound ions (in contradistinction to the free ions, the friction of which gives the joule electric heat). This resonance effect determines for each single period of the external electromotive force (*i.e.* the light) the two optical constants of the body, namely, the refractive index and the absorption coefficient. The index is connected with the quasi-elastic energy of the vibrating ions and therefore with their amplitude. The greater the amplitude of the resonance vibration, the greater the probability that the molecule will break up, that is, a greater part of the light will be effective in doing *chemical* work. So it seems that the *chemical* effectiveness of a wave length will depend on whether it is much refracted or not. Now the shortest wave lengths are most refracted, *i.e.* the system has the greatest refractive index for such, and hence short wave lengths, violet and ultra-violet, should be most photochemically active. This is a well-established fact. Further, with substances exhibiting an absorption band for wave lengths just below the band (*i.e.* a little longer than those absorbed) refraction occurs to an exceedingly great extent, such behaviour being called anomalous refraction. The dyestuffs (optical sensitisers) used to sensitise plates for colours, red, yellow, or green, etc., to which the silver salts are not sensitive themselves, possess this property of anomalous refraction, which fact is likewise in agreement with the principle that the waves which are most highly refractive are also most chemically active.

NOTE.—The numerical values quoted in the above account of Byk's theory have been criticised by Weigert (*Zeitsch. Elektrochem.*, **14**, 470, 1908) on the grounds that the choice of values for the calculation of the constants has been an unfortunate one. According to Weigert the factor α is really a constant independent of temperature, *cf.* below.

The Luther-Weigert Theory.

Weigert (*Zeitsch. physik. Chem.*, **63**, 458, 1908) has put forward some thermodynamical considerations of a very similar nature to those of Byk, for the investigation of the same experimental case, the photo-poly-

merisation of anthracene. After equating the free energy change δE to the work done in isothermally and reversibly decreasing the quantity of dianthracene δD in a mixture of A and D, *i.e.* the natural dark reaction, Weigert obtained—

$$\frac{\delta E}{\delta D} = VRT\left(\log \frac{[D]}{[A^2]} - \log \frac{[D_0]}{[A_0]^2}\right) \quad . \quad . \quad . \quad (1)$$

whence $\frac{[D_0]}{[A_0^2]}$ is the dark equilibrium constant $= K_0$

If we write $\frac{\delta E}{\delta D}$ as $\frac{dE}{dD}$ or as $\frac{dE}{dt} \cdot \frac{dt}{dD}$, and remembering that $\frac{dE}{dt}$ is simply the energy absorbed per second by A, *i.e.* the αE_A of Byk, then the above equation becomes—

$$\frac{dD}{dt} = \frac{\alpha E_A}{VRT\left(\log \frac{[D]}{[A^2]} - \log \frac{[D_0]}{[A_0^2]}\right)}$$

which is the same as Byk's equation (1) without the term kD. At low temperatures, as Byk himself (*Ber.*, **42**, 1145, 1909) has pointed out, k is very small, and kD is negligible, so that thermodynamically the two theories are identical. Weigert has used equation (1) in the integrated form—

$$E = VRT\left\{[D]\left(\log \frac{[D]}{[A^2]} - \log K_0\right) + ([A] + 2[D]) \log [A] + [D] + \text{constant}\right\} \quad . \quad . \quad (2)$$

and since for all practical purposes the definite integral between the dark equilibrium point and the given arbitrary dianthracene concentration is required, we can write this equation in the form—

$$E_D^{D_0} = VRT\left\{[D]\left(\log \frac{[D]}{[A^2]} - \log K_0\right) + ([A] + 2[D]) \log \frac{[A]}{[A] + 2[D]} + [D]\right\} \quad . \quad . \quad . \quad (3)$$

Further (*Ber.*, **42**, 850, 1909), Weigert concludes as a result of experiment that $\frac{dE}{dt}$ is a constant, as Byk had at *first* assumed to be the case for αE_A, and that therefore—

$$E = \frac{dE}{dt} t,$$

and this is to be introduced into the above expression instead of E. As already mentioned, Weigert has very carefully measured the *dark* equilibrium constant K_0 for $A \rightleftarrows D$ in toluene at 85° and 105° C., and it was found that raising the temperature favoured the existence of dianthracene. In fact, K_0 could be written as a function of the temperature thus—

$$\log K_0 = \frac{4330}{T} + 10{\cdot}27.$$

The following are some of Weigert's experimental results for reactions

exposed to light. Under the given conditions 0·007 calories per minute was the chemically active portion of the light energy, and knowing the value of K_0 it is possible to calculate the amount of D formed in photo-equilibrium by applying equation (3) above:—

Temperature.	log K_0.	Exposure in Minutes.	Initial Concentration of Anthracene.	D Calculated in Moles/Liter.	D Found in Moles/Liter.
65°	− 2·53	100	96	1·93	2·10
75°	− 2·15	60	42	1·07	1·00, 0·91, 0·92
75°		60	97	1·27	1·29, 1·20, 1·24
75°		100	63	1·84	1·86
85°	− 1·82	100	44	1·80	1·84, 1·82, 1·91, 1·74, 1·85, 1·85
85°		100	107	2·16	2·23, 2·19, 2·15, 2·14
105°	− 1·18	100	43	1·92	1·89, 1·78, 1·80, 1·98, 1·82, 1·78
105°	− 1·18	100	102	2·31	2·30, 2·26, 2·32, 2·25, 2·12, 2·15

The agreement between calculated and observed values of [D] is fairly good.

It will be remembered that Byk pointed out that the values of [D] and [A] in the photo-stationary state agreed well with that calculated on thermodynamic grounds in the region where [A] was fairly large. Weigert, on the other hand, has found (*Zeitsch. physik. Chem.*, 1908) that the agreement is good in the region of small [A] values, and suggests that the lack of agreement found by Byk is due to his unhappy choice of Weigert's data for the calculation of the constants in the formula. Weigert in the 1908 paper, therefore sees no necessity for introducing, as Byk has done, an electromagnetic (or, indeed, any other) explanation for this discrepancy. Whether there is a discrepancy or not must remain open at this stage. In his 1909 paper, however, Weigert again brings in the intermediate compound hypothesis. It should be remembered in this connection that an important fact, to which we have already referred, is made certain by Weigert's experiments, namely, that the concentration of D increases on adding more A, even when the amount of A already present is such that the light is completely absorbed, prior to the further addition of A being made. As Byk has pointed out, the thermodynamical theory (which was worked out independently and practically simultaneously by Byk and Weigert[1]) is not sufficient to

[1] It is not proposed here to discuss the relative merits of the contributions of each of these investigators to the subject of photochemistry. It is only fair to point out, however, that for all the experimental results we are indebted to Weigert, either alone or in collaboration with Luther.

explain this. Weigert and Luther suggested in 1908 (*Zeitsch. physik. Chem.*, **63**, 408, *seq.*, 1908) a chemical explanation of the fact that when the strength and thickness of the solution was such that the light absorption was nearly complete they found experimentally that, on further addition of anthracene, there was a still further increase in the dianthracene at the stationary state concentration. So that, for example, in an anthracene solution containing 20 millimoles per liter, the concentration of A in the photo-stationary state was only 50 per cent. of the maximal amount (which could be realised if a large quantity of anthracene were present), whilst at the same time the light-absorption was practically 100 per cent. in both cases. It is, therefore, necessary to distinguish between chemically and thermally absorbed light, for in the above instance only 50 per cent. of the light was photo-productive. *Further, they brought out the very important fact that the absorption of the D and solvent present could not account for such a great absorption, so that they assume the existence of one, or more, strongly thermally absorbent substances* produced from the A and which might be called D_1, which substance in turn can break down to give dianthracene.

A rise in temperature, according to the Le Chatelier-van 't Hoff principle, will favour the production of heat-absorbing substances—that is, of the hypothetical substance referred to—and therefore the rate of production of dianthracene will be favoured by rise of temperature, though it has been shown that the stationary state quantity D_l is actually diminished. The effect of temperature in thus altering the effectiveness of the light comes into the thermodynamical expression involving αE_A, which cannot be regarded as a constant independent of temperature and concentration. We thus have to regard the expression α as a variable (either on the basis of Byk's electromagnetic theory or Weigert's intermediate compound theory), in order to make the thermodynamic expression fit the facts. At present it would be useless to attempt to decide between these two opposing theories while the problem is still only in its early stages.

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